THE UNIVERSITY OF ALBERTA

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TITLE OF THESIS

DEGREE FOR WHICH THESIS WAS PRESENTED

YEAR THIS DEGREE GRANTED

THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR .Leon Frederick Doty..................

TITLE OF THESIS .Fluoro and Trifluoromethyl Phosphorus

.Compounds......................................

....

DEGREE FOR WHICH THESIS WAS PRESENTED ...Ph.D............

YEAR THIS DEGREE GRANTED ....1973....................

THE UNIVERSITY OF ALBERTA

FLUORO AND TRIFLUOROMETHYL PHOSPHORUS COMPOUNDS

BY

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1973

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"FLUORO AND TRIFLUOROMETHYL PHOSPHORUS COMPOUNDS"

submitted by LEON FREDERICK DOTY in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

TO MOM, DAD AND FAE

A B S T R A C T

Two new diphosphorus compounds, difluorothiophosphoryl-μ-thiobis(trifluoromethyl)phosphine and bis(trifluoromethyl)-thiophosphoryl-μ-thiodifluorophosphine have been shown by nmr and chemical studies to adopt a structure wherein one phosphorus atom is trivalent and the other is pentavalent. The second of these compounds shows temperature dependent behaviour in its nmr spectrum which is consistent with an intermolecular exchange process of undetermined molecularity. This type of mechanism has been substantiated by chemical exchange studies.

The new compound fluoro(trifluoromethyl)dithiophosphinic acid has been prepared. This compound and $CF_3(F)PN(CH_3)_2$ have facilitated the completion of the series of fluoro and trifluoromethyl substituted thiophosphoryl-μ-thiophosphines. The nmr spectra of these compounds have, in most cases, been fully analysed and the presence of an asymmetric phosphorus atom in these molecules has permitted the measurement of geminal F-F and CF_3-CF_3 coupling constants for groups joined to phosphorus. Two asymmetric centres in one molecule are observed in fluoro(trifluoromethyl)thiophosphoryl-μ-thio fluoro(trifluoromethyl)phosphine which is found to exist as an unseparated mixture of two racemates. Systematic variations in the nmr parameters for all members of this series have been rationalized by considering electronegativity and π bonding effects of the substituents on these molecules.

Attempts to prepare trifluoromethyl-iodo-phosphines from P_2I_4 and CF_3I were unsuccessful but led to convenient methods of increasing the degree of trifluoromethyl substitution of phosphines from one or two to three. These methods have also yielded a convenient synthetic route to $(CF_3)_2PCH_3$ from which a new five coordinate phosphorane $(CF_3)_2P(CH_3)Cl_2$ and a new thiophosphoryl compound $(CF_3)_2P(S)CH_3$ have been derived. The anionic species resulting from the hydrolysis of $(CF_3)_2PCH_3$, $(CF_3)_2P(S)CH_3$, $(CF_3)_2PSP(CF_3)_2$ and $(CF_3)_2POP(CF_3)_2$ have been observed in the nmr.

ACKNOWLEDGEMENTS

The author expresses thanks to his research supervisor, Dr. R. G. Cavell for assistance and direction during the course of these studies and to members of Dr. Cavell's research group for many helpful discussions and suggestions.

The advice and assistance offered by Dr. R. E. D. McClung, on many nmr problems, is gratefully acknowledged and the author wishes to thank Dr. Cavell, Dr. McClung, Dr. R. B. Jordan and Dr. A. J. Tomlinson for their invaluable comments after reading this manuscript.

Much gratitude is due to the competent technical staff in the Department of Chemistry, especially to Mr. T. Brisbane, Dr. T. Nakashima, Mrs. D. Formanski, and Mrs. M. Tychkowsky.

The author also thanks Mrs. M. Waters for her able and speedy preparation of this manuscript and Mr. G. Johanson for drafting of the many diagrams which appear.

Last, but certainly not least, financial assistance from the University of Alberta and the National Research Council of Canada is gratefully acknowledged.

TABLE OF CONTENTS

Page

CHAPTER 1

INTRODUCTION 1

CHAPTER 2

MATERIALS, APPARATUS, AND TECHNIQUES 11

High vacuum system and techniques 11

Reaction conditions 12

Materials 12

Instrumental techniques 12

CHAPTER 3

PREPARATION, CHARACTERIZATION, AND NMR STUDIES OF TWO NEW MIXED VALENCE COMPOUNDS 15

Introduction 15

Experimental 17

Preparation of $(CF_3)_2P\text{-}S\text{-}P(S)F_2$ 17

Reactions of $(CF_3)_2P\text{-}S\text{-}P(S)F_2$ 17

Preparation of $F_2PSP(S)(CF_3)_2$ 20

Reactions of $F_2PSP(S)(CF_3)_2$ 20

Reaction of $(CF_3)_2P(S)SP(CF_3)_2$ with dimethylamine. 23

Reactions of $F_2P(S)SPF_2$ 24

Preparation of difluorodithiophosphinic acid 25

Results and Discussion 26

Synthesis of $F_2P(S)SP(CF_3)_2$ and $(CF_3)_2P(S)SPF_2$ 26

Page

Chemical reactions of the mixed valence compounds 28

Nmr spectra of $F_2P(S)SP(CF_3)_2$ and $(CF_3)_2P(S)SPF_2$ 31

Molecular exchange phenomena and thermal stability 43

CHAPTER 4

MIXED VALENCE COMPOUNDS WITH ASYMMETRIC PHOSPHORUS CENTRES 47

Introduction 47

Experimental 50

Reactions of $CF_3(F)PN(CH_3)_2$ 50

Reactions of the solid residue from $CF_3(F)PN(CH_3)_2 + H_2S$ 51

Reactions of $CF_3(F)P(S)N(CH_3)_2$ 52

Reaction of $CF_3(F)PS_2^-$ with H_2SO_4 53

Preparation of $CF_3P(S)F_2$. 54

Preparation of $CF_3(F)P(S)SP(CF_3)_2$ 55

Reactions of $CF_3(F)P(S)SP(CF_3)_2$ 55

Preparation of $CF_3(F)P(S)SPF_2$ 55

Reactions of $CF_3(F)P(S)SPF_2$ 56

Preparation of $(CF_3)_2P(S)SP(F)CF_3$ 56

Reactions of $(CF_3)_2P(S)SP(F)CF_3$ 57

Preparation of $F_2P(S)SP(F)CF_3$ 57

Reactions of $F_2P(S)SP(F)CF_3$ 58

Preparation of $CF_3(F)P(S)SP(F)CF_3$ 58

Page

Results 59

Synthesis and Chemistry of $CF_3(F)P(S)SH$ and related compounds 59

Nmr studies of mixed valence compounds containing chiral centres 63

$CF_3(F)P(S)SP(CF_3)_2$ 65

$CF_3(F)P(S)SPF_2$ 74

$(CF_3)_2P(S)SP(F)CF_3$ 82

$F_2P(S)SP(F)CF_3$ 91

$CF_3(F)P(S)SP(F)CF_3$ 101

Discussion 112

Geminal non-equivalence in mixed valence compounds with chiral phosphorus centres 112

Systematic variations in the nmr parameters of the mixed valence compounds . . 114

The ^{31}P nmr spectrum of trivalent phosphorus in $F_2P(S)SP(F)CF_3$. 123

CHAPTER 5

REACTIONS OF COMPOUNDS CONTAINING P-P BONDS WITH CF_3I AND CH_3I AND RELATED CHEMISTRY 128

Introduction. 128

Experimental. 131

Reactions of CF_3I 131

Reactions of CH_3I 132

Reactions of $(CF_3)_2PCH_3$ 133

Reactions of $(CF_3)_2P(S)CH_3$. 135

Fluorination of $(CF_3)_2P(CH_3)Cl_2$ 136

Page

Reaction of $(CF_3)_3PS$ with $(CH_3)_2NH$ 136

Reactions of $(CF_3)_2PSP(CF_3)_2$ 137

Reactions of $(CF_3)_2POP(CF_3)_2$ 138

Results and Discussion 140

CHAPTER 6

CONCLUSIONS 147

REFERENCES 152

LIST OF TABLES

TABLE		PAGE
1	Coupling and Chemical Shift Parameters of Mixed Valence Compounds.	27
2	Nmr Spin States of Exchanging Species in $CF_3)_2P(S)SPF_2$.	39
3	Chemical Exchange of Mixed Valence Compounds.	44
4	Nmr Coupling and Chemical Shift Parameters for $(CF_3(F)P(S)SP(CF_3)_2$ (V).	72
5	Nmr Coupling and Chemical Shift Parameters for $CF_3(F)P(S)SP(CF_3)_2$ (VI).	80
6	Nmr Coupling and Chemical Shift Parameters for $(CF_3)_2P(S)SP(F)CF_3$ (VII).	83
7	Nmr Coupling and Chemical Shift Parameters for $F_2P(S)SP(F)CF_3$ (VIII).	92
8	Nmr Coupling and Chemical Shift Parameters of the Major Component of the Mixture of the Isomers of $CF_3(F)P(S)SP(F)CF_3$ (IX).	103
9	Nmr Coupling and Chemical Shift Parameters of the Minor Component of the Mixture of the Isomers of $CF_3(F)P(S)SP(F)CF_3$ (X).	104
10	Collected Nmr Coupling Parameters for the Series of Mixed Valence Compounds $^1J_{FP}$, $^2J_{FP}$ and J_{FF}^{gem}.	115
11	Averaged Nmr Parameters for the Series of Mixed Valence Compounds.	117

TABLE		PAGE
12	Collected Chemical Shift Parameters for the Series of Mixed Valence Compounds.	120
13	Collected Nmr Coupling Parameters for the Series of Mixed Valence Compounds $^4J_{FP}$, $^3J_{FP}$, and $^2J_{PP}$.	122

LIST OF FIGURES

FIGURE		PAGE
1	The series of fluoro and trifluoromethyl substituted thiophosphoryl-μ-thiophosphine mixed valence compounds and their numbering scheme.	8
2	^{31}P temperature dependent nmr spectrum of $(CF_3)_2P(S)SPF_2$ and the calculated first order pattern in the absence of exchange.	35
3	Theoretical lineshapes of the ^{31}P spectra of $(CF_3)_2P(S)SPF_2$ at exchange rates varying from 0.001 to 10,000 sec^{-1}.	42
4	Neuman projections of the rotamers of $CF_3(F)P(S)SP(CF_3)_2$ (V).	64
5	Observed and calculated ^{19}F and ^{31}P nmr spectrum of $CF_3(F)P(S)SP(CF_3)_2$ (V).	67-71
6	Observed and calculated ^{19}F and ^{31}P nmr spectrum of $CF_3(F)P(S)SPF_2$ (VI).	76-79
7	Observed and calculated ^{19}F and ^{31}P nmr spectrum of $(CF_3)_2P(S)SP(F)CF_3$ (VII).	86-90
8	Observed and calculated ^{19}F and ^{31}P nmr spectrum of $F_2P(S)SP(F)CF_3$ (VIII).	94-99
9	Neuman projections of the isomers of $CF_3(F)P(S)SP(F)CF_3$ (IX and X).	102
10	Observed and calculated partial ^{19}F and ^{31}P spectra of the isomers of $CF_3(F)P(S)SP(F)CF_3$ (IX and X).	106-108

FIGURE		PAGE
11	High field half of ^{31}P spectrum of P^{III} in $F_2P(S)SP(F)CF_3$.	124
12	Partial energy level diagram of $F_2P(S)SP(F)CF_3$ showing some allowed transitions.	126

CHAPTER 1

INTRODUCTION

The chemistry of compounds of phosphorus containing highly electronegative groups has received much attention in the past 20-30 years. Although the simple fluorides PF_3, PF_5, OPF_3, and SPF_3 were prepared prior to 1900, it was many years before there was any further activity in the field. One of the major reasons for the increased interest was the discovery of the so-called nerve gases in the 1930's which were found to inhibit the enzyme cholinesterase.[1] These organophosphorus fluorides were synthesized in great number for their military application and also added impetus to further study of phosphorus fluorides. In 1953, it was found that the recently prepared CF_3I [2] reacted with elemental phosphorus at elevated temperatures to give trivalent phosphorus compounds substituted with trifluoromethyl groups.[3] This grouping has an electronegativity somewhere between those of fluorine and chlorine.[4] The trifluoromethyl group has the benefit of remaining attached to phosphorus and not migrating as the simple halides do.[5] Since that time, many new compounds of phosphorus containing fluorine and trifluoromethyl groups have been prepared. An extensive review of the chemistry of the fluoro compounds has been presented by Schmutzler in 1965 [1], and the trifluoromethyl compounds

have been reviewed somewhat less completely as recently as 1969.[4-7] References to specific aspects of phosphorus chemistry will be presented in the course of the text.

The rationale for the study of these types of compounds lies in their dissimilarity to classical organophosphorus species. An important synthetic route in organophosphorus chemistry is the Arbuzov reaction.[8] This involves reactions of a trialkylphosphite or dialkylphosphonite with an alkyl halide according to equation 1.

$$(RO)_3P + R'X \longrightarrow (RO)_3P^+ - R'X^- \longrightarrow (RO)_2P(=O)R' + RX \qquad (1)$$

Here the trivalent phosphorus is oxidized to its pentavalent phosphine oxide analog, with elimination of an alkyl group from the phosphite or phosphonite starting material as RX and formation of a bond from phosphorus to the alkyl group of R'X. Burg gives several examples in the trifluoromethyl systems where the Arbuzov reaction is not observed.[5] Heating $(CF_3)_2P(OBu^t)$ with CH_3I resulted in oxidation of the phosphorus but no methyl groups were attached; a non-Arbuzov reaction. Griffiths and Burg have also reported "anti-Arbuzov" behaviour in the attempted synthesis of $(CF_3)_2P(O)H$.[9] Although it is thought that the desired compound was initially formed, it was necessary to postulate

a rearrangement in which P^{V} was reduced to P^{III} in order to explain the formation of $(CF_3)_2POH$. Also obtained were $(CF_3)_2PH$ and $(CF_3)_2P(O)OH$, presumably due to a mutual oxidation reduction reaction.

$$(CF_3)_2P(O)H \longrightarrow (CF_3)_2POH \qquad (2)$$

$$2(CF_3)_2P(O)H \longrightarrow (CF_3)_2PH + (CF_3)_2P(O)OH \qquad (3)$$

The disproportionation reaction is the only reaction which the methyl analogue undergoes.[9]

$$(CH_3)_2P(O)H \longrightarrow (CH_3)_2PH + (CH_3)_2P(O)OH \qquad (4)$$

This work has been substantiated and extended by others and it is now well established that the trifluoromethyl compounds $(CF_3)_2POH$ and $(CF_3)_2PSH$ [10] exist only in the trivalent phosphorus form whereas alkyl and phenyl phosphinic acids exist exclusively in the $R_2P(O)H$ [11] form.

When joined to phosphorus, both CF_3 and F, because of their very high electronegativities, are thought to contract and lower the energy of the phosphorus 3d orbitals making them available for bonding.[5,12] In general 3d orbitals are not available for bonding in organophosphorus compounds and this perhaps explains the non-existence of PH_5 and the existence of PF_5 in both of which d orbitals are thought to be necessary. The poor Lewis base character of the fluoro and trifluoromethyl derivatives of phosphorus

in contrast to their organophosphine counterparts [5] is also the result of the high electronegativity of these substituents.

Another feature of the fluoro and trifluoromethyl compounds of phosphorus which makes them attractive for study is their generally high volatility. Since many of the systems, especially the trivalent phosphines with CF_3 groups attached, are rapidly oxidized by air and hydrolysed by moisture [13], they must be handled using standard high vacuum techniques.

The presence of phosphorus and fluorine atoms, both of which have nuclear spins of 1/2, permits nmr studies of these compounds. Although ^{19}F, ^{31}P, and ^{1}H are all present in essentially 100% natural abundance, the sensitivity of the nmr technique is 6% for ^{31}P and 83% for ^{19}F compared to 100% for ^{1}H due to the different magnetogyric ratios for the three nuclei.[14] Nmr spectra of the ^{19}F nucleus have long been easily obtainable in these compounds but ^{31}P spectra have generally only been obtained with some difficulty due to the low sensitivity of this nucleus and the extensive splitting it suffers due to coupling with other magnetic nuclei in the molecule. Recently the availability of Fourier transform nmr spectroscopy [15] has allowed measurement of ^{31}P spectra of high quality from small samples of these compounds where extensive splitting causes the spectrum to span a large frequency range. Another

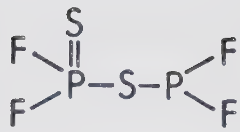
advance has been the development of nmr instruments which can be locked on a nucleus different from the one being observed. Lock systems, both homonuclear and heteronuclear, are used to stabilize the magnetic field of the spectrometer over the period of time required for the nmr experiment. The heteronuclear lock system has proved invaluable in measuring low temperature ^{31}P spectra since lock compounds containing phosphorus which are useful at low temperatures are not readily available.

In both fluorinated and trifluoromethylated phosphorus compounds, large chemical shift differences between non-equivalent nuclei are generally observed in both ^{19}F and ^{31}P spectra. As well, short range spin-spin coupling constants are large and are often indicative of the oxidation state and coordination about the phosphorus atom.[16] For example, in trifluoromethylated phosphorus compounds, $^{2}J_{FP}$ generally ranges from 60-90 Hz for trivalent phosphines [16], from 100-140 Hz for pentavalent four coordinate compounds [16], and may be less than 50 Hz for axial groups and more than 150 Hz for equatorial groups on five coordinate phosphoranes.[16] The magnitude of coupling constants drops off rapidly as the range of coupling is increased. This behaviour together with the large chemical shift differences usually allows first order analysis of the nmr spectra of these compounds.

The nucleophilic attack of hydroxide ion on trifluoro-

methylated phosphorus quantitatively cleaves carbon-phosphorus linkages to give fluoroform and has been recognized as a valuable analytical tool.[3] The number of these bonds which are ruptured depends not only on how many trifluoromethyl groups are attached but also on the oxidation state of the phosphorus and the nature of the other substituents which are present. Phosphines, on alkaline hydrolysis, eliminate all bound CF_3 groups as fluoroform, although electropositive substituents tend to inhibit this elimination.[17] In phosphoryl and thiophosphoryl compounds, one CF_3 group remains attached to phosphorus on alkaline hydrolysis.[10,18,19] Neutral hydrolysis of phosphines leaves one CF_3 group bound to phosphorus [13,20], while two groups remain attached in phosphoryl and thiophosphoryl compounds.[19] These reactions have no parallels in organophosphorus chemistry.

The original aims of the work described in this thesis were further understanding of thiophosphoryl-μ-thiophosphines (hereafter referred to as mixed valence compounds) and to develop new synthetic routes to trifluoromethylated phosphorus compounds. Charlton reported the first of the mixed valence compounds, difluorothiophosphoryl-μ-thio-difluorophosphine [21] ($F_2P(S)SPF_2$(I)), and soon after the trifluoromethylated analog [$(CF_3)_2P(S)SP(CF_3)_2$ (II)] [22] was prepared. These two compounds and the new mixed valence compounds reported in this thesis and their numbering scheme are shown in Figure 1. The two original compounds (I and II) were



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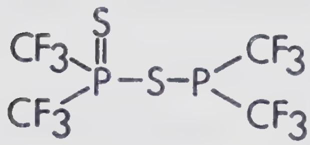

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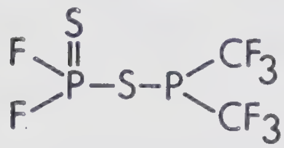

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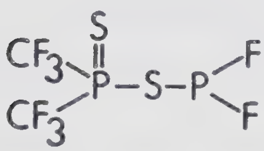

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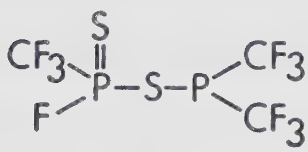

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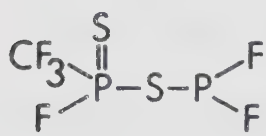

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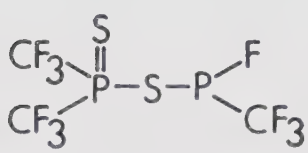

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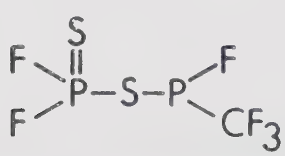

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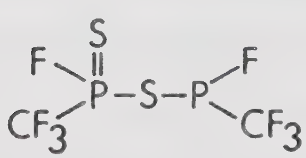

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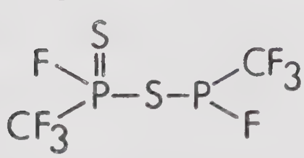


X

FIGURE 1. The series of fluoro and trifluoromethyl substituted thiophosphoryl-μ-thiophosphine mixed valence compounds and their numbering scheme.

interesting inasmuch as a formal +3 oxidation state could be assigned to one of the phosphorus atoms while the other was found to be pentavalent. These structures were postulated on the basis of nmr and ir assignments, chemical properties, and, in the case of the trifluoromethylated compound, its behaviour on alkaline hydrolysis. Although the trifluoromethylated compound (II) showed a well resolved nmr spectrum at room temperature, the nmr spectrum of the fluorinated species (I), even at the low temperature limit of the instrument, was not completely resolved. This temperature dependence could be explained on the basis of a chemical exchange process of several possible origins:

(1) possible exchange of the double bonded sulfur from one phosphorus atom to the other.

(2) rotation about either or both of the P-S single bonds.

(3) exchange of part of the molecule between two or more molecules.

Two new mixed valence compounds difluorothiophosphoryl-μ-thiobis(trifluoromethyl)phosphine (III) and bis(trifluoromethyl)thiophosphoryl-μ-thiodifluorophosphine (IV) substituted with two trifluoromethyl groups on one of the phosphorus atoms and two fluorine atoms on the other were synthesized in an attempt to rule out some of these alternatives and the

results of this investigation are reported in Chapter 3.

Synthesis of the two compounds difluorodithiophosphinic acid (F_2PS_2H)[23] and bis(trifluoromethyl)dithiophosphinic acid $(CF_3)_2PS_2H$[10,18] made possible the preparation of the mixed valence compounds described above (I, II, III, IV) as well as $F_2P(S)SP(F)CF_3$ (VIII) and $(CF_3)_2P(S)SP(F)CF_3$ (VII). Chapter 4 describes the synthesis of fluorotrifluoromethyldithiophosphinic acid ($CF_3(F)PS_2H$), the preparation of the latter two compounds (VII, VIII) and of $CF_3(F)P(S)SPF_2$ (VI), $CF_3(F)P(S)SP(CF_3)_2$ (V), and $CF_3(F)P(S)SP(F)CF_3$ (IX, X) from the new acid. These new compounds have allowed the measurement of geminal F-F and CF_3-CF_3 nmr coupling constants which are also reported in Chapter 4.

The second project, which is described in Chapter 5, was undertaken in an attempt to find a cleaner synthesis for the trifluoromethylphosphine starting materials with higher hields than the one described in 1953.[3] Previous investigations[24] showed that both trifluoromethyl iodide and methyl iodide reacted with tetrakistrifluoromethyl diphosphine to give $(CF_3)_2PI$ and $(CF_3)_3P$ or $(CF_3)_2PCH_3$ and $(CF_3)_2PI$ respectively and it seemed reasonable to expect P_2I_4[25] to undergo the same type of reaction. The P-P bond proved to be resistant to cleavage and this route to CF_3P compounds did not materialize; however improved methods of adding CF_3I and CH_3I to $(CF_3)_2PP(CF_3)_2$ as well

as to $(CF_3P)_{4,5}$ [27] cyclic phosphines were developed. This has facilitated the increase in the number of trifluoromethyl substituents of mono- and di- CF_3 substituted phosphines. Previous results of Leary demonstrated the feasibility of decreasing the CF_3 substitution on phosphorus from 3 to 2 and this work has been extended in this Chapter. Subsequent to this work it was found possible to synthesize a methylene bridged diphosphine by reaction of CH_2I_2 and Hg with the diphosphine.[28] Chapter 5 also describes the identification of the unreported anions $CH_3(H)PO_2^-$ and $CF_3(CH_3)PO_2^-$ from the hydrolysis of the parent compounds.

CHAPTER 2

MATERIALS, APPARATUS, AND TECHNIQUES

The materials, apparatus, and techniques described in this Chapter were generally used in the course of this investigation. Any special techniques or apparatus will be described more fully where applicable.

(1) High vacuum system and techniques

Due to the sensitivity of many of the starting materials and products of reactions to air and moisture, all manipulations of volatile compounds were carried out in a standard Pyrex vacuum system. An ultimate pressure of less than 10 microns of mercury was attainable by use of a mercury diffusion pump separated from the main vacuum system by a cold trap held at -196°C and backed by a rotary oil pump. Various parts of the system were isolated by high vacuum glass stopcocks lubricated with Apiezon N grease. Separation of volatile compounds was effected by passage through a series of U-traps cooled by slush baths at various temperatures and often final purification was facilitated by use of a micro reflux column which has been described previously.[29] Pressure measurements were made using mercury manometers or in the case of compounds that reacted with mercury, an all glass microtensiometer. Often vacuum distillations were monitored by a Pirani gauge which was also used to measure the background pressure of the

system.

(2) Reaction conditions.

Most reactions were carried out in Pyrex tubes of 10, 25 or 75 ml volume although those expected to generate high pressures (>3 atm) were performed in quartz Carius tubes of about 50 ml volume. In the initial part of this study, the trifluoromethyl phosphine starting materials were prepared from CF_3I, phosphorus, and iodine in Carius tubes heated in a tube oven at 210°C. Later a 500 ml stainless steel bomb fitted with a large heatable valve was used. This bomb was heated in a large bath of silicone oil. For reactions which could occur in more than one stoichiometry, such as the addition of dimethylamine to PF_3, a gas phase reactor was used.

(3) Materials.

All compounds which were not commercially available were prepared by literature methods. Reagent grade commercially available materials generally were fractionated before use to remove impurities or, if this was not possible, were pumped on to remove moisture and air.

(4) Instrumental techniques.

Where possible both starting materials and new compounds were routinely checked for purity by infrared or nuclear magnetic resonance spectroscopy. The infrared in-

struments used included the Perkin Elmer 337, 457 and 421 spectrometers. Routine purity checks by nmr were accomplished using the Varian A60 or A 56/60A instruments. The former operated at 60 MHz for proton spectra and the latter spectrometer, operating at 56.4 MHz for fluorine nuclei and 60 MHz for protons, was equipped with a Varian V6040 temperature controller and was used for preliminary studies of temperature dependent spectra. Higher resolution spectra were obtained on a Varian HA 100 instrument, also equipped with a V6040 temperature controller, but capable of attaining temperatures as low as about -120°C. This spectrometer operates at 100 MHz for protons, 94.1 MHz for fluorine and 40.5 MHz for phosphorus nuclei. Since the Varian system is unsatisfactory for recording ^{31}P spectra at low temperatures due to the difficulty in finding a good low temperature lock compound, the Bruker HFX90 system with Fourier transform capability and heteronuclear lock was used for low temperature studies. This system operates at 90 MHz for protons, 84.6 MHz for fluorine, and 36.4 MHz for phosphorus nuclei. The phosphorus spectra were run in fluorinated solvents such as $CFCl_3$ or CF_2Cl_2 which also doubled as the lock compound. All phosphorus spectra were run in Fourier transform mode on this spectrometer and either 5000 or 10000 Hz sweep widths were collected in either 8K or 16K data points on the Nicolet 1085 computer associated with the system. Good quality spectra were

generally obtainable after 250 to 1000 input pulses depending on the concentration of the sample and the number of lines in the pattern. Spectra of the phosphorus nuclei which are reproduced in this thesis are expansions of the 5000 or 10000 Hz sweep width. Volatile samples for nmr were prepared under vacuum in 5 mm diameter tubes and were generally about 25% by volume in $CFCl_3$ or CF_2Cl_2. Fluorine chemical shifts are measured relative to $CFCl_3$ unless otherwise specified while phosphorus chemical shifts are given relative to neat P_4O_6. These latter values are not very accurate, especially at low temperatures, since the position of the P_4O_6 resonance can be measured only at room temperature and because the resonance frequency of the lock compound (CF_2Cl_2) is very temperature dependent. Nmr spectra of solid compounds were obtained in either water or CD_3CN and were prepared in the atmosphere. Terminology used in descriptions of nmr spectra and techniques may be found in many textbooks such as that by Emsley, Feeney, and Sutcliffe.[14]

Mass spectra were obtained on the AEI MS9 mass spectrometer, operating at an ionizing voltage of 70 eV, and were introduced as gases using a heated inlet system.

CHAPTER 3

PREPARATION, CHARACTERIZATION, AND NMR STUDIES OF TWO NEW MIXED VALENCE COMPOUNDS

INTRODUCTION

The recently prepared compounds $F_2P(S)SPF_2$ (I) [21] and $(CF_3)_2P(S)SP(CF_3)_2$ (II) [22] have been shown to have a structure which is unusual in phosphorus chemistry. The tetramethyl analog of these compounds $[(CH_3)_2P(S)P(S)(CH_3)_2]$ which has been the subject of a great deal of discussion in the literature [30], has been found to adopt a structure wherein both phosphorus atoms are pentavalent [30] while the fluoro and trifluoromethyl compounds have one phosphorus atom in the pentavalent form and the other in a trivalent form.[21,22] This behaviour is not completely unprecedented however, as tetramethyl diarsenic disulfide is reported to favor the latter structure.[31,32]

Other diphosphorus compounds containing the highly electronegative groupings CF_3 or F, and either oxygen or sulfur include the monosulfides and monoxides $((CF_3)_2P)_2S$ [41] $((CF_3)_2P)_2O$ [33], $(F_2P)_2S$ [34], and $(F_2P)_2O$.[35,36] These are all found to be symmetrical compounds with both phosphorus atoms in their trivalent oxidation state and a sulfur or oxygen atom bridging the two phosphorus atoms. Examples of fluorophosphorus compounds containing two pentavalent phosphorus atoms include $(SPF_2)_2S_x$ (x = 1[37], 2[38], 3[38], 4[38])

and $(SPF_2)_2O$.[37] Trifluoromethyl substituted compounds of this type include $(CF_3)_2P(S)SSP(S)(CF_3)_2$ [22] and $(CF_3)_2P(S)OP(S)(CF_3)_2$.[23] Attempts to synthesize $(CF_3)_2P(S)SP(S)(CF_3)_2$ [22] have proved unsuccessful and have resulted in the formation of the mixed valence compound $(CF_3)_2P(S)SP(CF_3)_2$.

The fully trifluoromethylated compound (II) has been shown to be very stable and to undergo reaction mainly at the P^{III}-S bond. It showed all the possible nmr couplings at room temperature and the nmr spectrum seemed to be invariant with temperature.[22] The fluorinated compound, $F_2P(S)SPF_2$ (I), on the other hand, was not particularly stable at room temperature and eliminated PF_3. Like the CF_3 substituted compound, compound I too underwent reactions at the P^{III}-S bond but unlike II showed a temperature dependent nmr spectrum which was not resolved at room temperature.[21] This latter phenomenon suggested the possibility of an environmental exchange process occurring within the molecule. This Chapter reports the synthesis of two new mixed valence compounds, $F_2PSP(S)(CF_3)_2$, and $(CF_3)_3PSP(S)F_2$ their chemical characterization, and nmr studies which have elucidated some features of the nature of the exchange process.

EXPERIMENTAL

Preparation of $(CF_3)_2P\text{-}S\text{-}P(S)F_2$ (III)

Difluorothiophosphoryl-μ-thio-bis(trifluoromethyl)-phosphine was prepared in almost quantitative yield from the reaction of stoichiometric amounts of SPF_2SH and $(CF_3)_2PN(CH_3)_2$. In a typical reaction 3.429 gm (25.6 mmoles) of SPF_2SH and 2.630 gm (12.35 mmoles) of $(CF_3)_2PN(CH_3)_2$ reacted instantaneously at room temperature in a sealed tube to produce 3.677 gm (12.2 mmoles) (98.7% yield) of pure $(CF_3)_2PSP(S)F_2$, which was trapped at -63°C. A mixture of III and SPF_2SH (0.160 gm) passed through this trap and an undetermined amount of solid identified as $F_2PS_2^-$ $(CH_3)_2NH_2^+$ by nmr spectroscopy remained in the reaction tube.

Reactions of III

(1) Alkaline hydrolysis

Compound III (0.1562 gm; 0.518 mmoles) was shaken with a large excess of 10% aqueous NaOH for 3 hr at room temperature. The only volatile product was fluoroform (0.0751 gm; 1.073 mmoles) identified by infrared spectroscopy.

(2) With anhydrous hydrogen chloride

III (0.472 gm; 1.56 mmole) was reacted in a sealed tube for 10 days at room temperature with 0.105 gm (2.88 mmole) of anhydrous HCl. Separation of the volatile pro-

ducts gave a mixture of SPF_2SH (0.268 gm) and III (trapped at -96°C). The fraction collected at -130°C contained 0.248 gm (1.21 mmole) of $(CF_3)_2PCl$ contaminated with a trace of III and at -196°C 0.0602 gm (1.65 mmole) of HCl containing traces of SiF_4 and $(CF_3)_2PCl$ was found.

(3) With dimethylamine

To 0.1602 gm (0.53 mmole) of III was added 0.0548 gm (1.22 mmole) of anhydrous dimethylamine. An immediate reaction ensued with formation of a white solid material. After 2 days at room temperature the only volatile product obtained was $(CF_3)_2PN(CH_3)_2$ (0.100 gm; 0.47 mmoles). The white solid residue was found by nmr spectroscopy to be $(CH_3)_2NH_2^+S_2PF_2^-$.

(4) Thermal behaviour

III (0.1608 gm; 0.532 mmoles) was heated at 200°C for 3 days in a sealed tube. The volatile material (0.1594 gm, 0.528 mmoles based on III) was found to be almost pure III contaminated with less than 1% of an unidentified contaminant (by nmr). A small amount of an unidentified crystalline solid (1.4 mg) remained in the reaction tube.

(5) With methyl mercaptan

III (0.282 gm, 0.93 mmoles) was sealed in a glass tube with CH_3SH (0.0504 gm; 1.05 mmole) and allowed to react overnight at room temperature. The volatile products

were fractionated and identified as CH_3SH (0.0034 gm; 0.07 mmole) plus an unseparated mixture of SPF_2SH and $(CF_3)_2PSCH_3$ (0.3266 gm). The nmr spectrum indicated that the latter two products were present in the approximate molar ratio 1:1.

(6) With mercury

The reaction of III (0.179 gm; 0.593 mmoles) with excess mercury (0.125 gm; 0.626 mmole) for 7 days at room temperature with shaking yielded $(CF_3)_2PP(CF_3)_2$ which was identified by nmr spectroscopy, and $Hg(S_2PF_2)_2$ which was identified by its mass spectrum and mass measurement of the molecular ion (found m/e = 467.8002; calc. m/e 467.8002).

(7) With anhydrous methanol

Methanol, dried by addition of sodium metal (0.0254 gm; 0.794 mmoles) was reacted with III. A complex mixture of products resulted. The major trifluoromethyl containing components were $(CF_3)_2PSH$ and $(CF_3)_2POCH_3$ in the approximate molar ratio 4:3 by nmr spectroscopy. A small amount of SPF_2SH was also observed along with 8 or 10 other compounds (by nmr) in smaller amounts which could not be identified. No further studies were undertaken.

(8) With chlorine

Chlorine gas (0.0466 gm; 0.657 mmoles) was reacted with III (0.1970 gm; 0.653 mmole) in a sealed tube at room

temperature. A complex mixture of products was obtained which was not separated since all species but one could be readily identified by nmr spectroscopy. The volatile products were found to be unreacted III (1%), $(CF_3)_2PCl$ (25%), $(CF_3)_2PCl_3$ (27.5%), SPF_2Cl (1.5%), and a species which is best formulated as $(SPF_2)_2S_2$ (45%) but may be one of the related polysulfides $(SPF_2)_2S_x$ $(x > 2)$ since nmr parameters are very similar for the $x \geq 2$ series.[38] Clearly $x \neq 1$.

Preparation of $F_2PSP(S)(CF_3)_2$ (IV)

Bis(trifluoromethyl)thiophosphoryl-μ-thiodifluorophosphine was prepared from the reaction of stoichiometric amounts of $(CF_3)_2PS_2H$ and $PF_2N(CH_3)_2$. In a typical reaction 2.63 gm (11.24 mmole) of $(CF_3)_2PS_2H$ was combined with 0.64 gm (5.63 mmole) of $PF_2N(CH_3)_2$ to yield 0.681 gm (2.26 mmole) of pure IV and an undetermined amount of solid $(CF_3)_2PS_2^-$ $(CH_3)_2NH_2^+$ which was identified by its nmr spectrum. The product was best purified by passage through a series of traps held at -45, -84 and -196°C followed by vacuum distillation of the -84° fraction in a low temperature micro reflux still maintained at -63°C.[29] The separation process is rather inefficient and yield of pure material is low.

Reactions of IV

(1) Alkaline hydrolysis

To an excess of 10% NaOH was added 0.362 gm (1.16

mmole) of IV. After overnight reaction at room temperature, the only volatile product was fluoroform (0.0846 gm; 1.21 mmole).

(2) <u>With anhydrous hydrogen chloride</u>

IV (0.241 gm; 0.80 mmole) was combined in a sealed tube with HCl (0.0305 gm; 0.84 mmole) and allowed to react for 6 days at room temperature. Separation of the volatile products gave $(CF_3)_2PS_2H$ (0.176 gm; 0.76 mmole) and PF_2Cl contaminated with a trace of PF_3 (0.0781 gm; 0.75 mmole). A small amount of unidentified product (15 mg) was also obtained.

(3) <u>With anhydrous dimethylamine</u>

To IV (0.232 gm; 0.77 mmole) was added $(CH_3)_2NH$ (0.071 gm; 1.57 mmole). There was an immediate reaction on warming the tube to room temperature with formation of a white solid. The volatile product was identified as $PF_2N(CH_3)_2$. The residual white solid was identified by nmr spectroscopy as $(CF_3)_2PS_2^-$ $(CH_3)_2NH_2^+$ (0.211 gm; 0.76 mmole).

(4) <u>Thermal behaviour</u>

IV (0.204 gm; 0.68 mmole) was heated in a sealed tube for 24 hr at 70°C and then for 2 hr at 100°C. Fractional distillation of the volatile products yielded PF_3 (0.014 gm; 0.16 mmole) and a mixture (0.169 gm) analysed

by ^{19}F nmr as II (38%), III (51%), and IV (11%). Compound I was not observed in the nmr perhaps as a result of low intensity due to low concentration plus its small F content; however it is likely to be unstable under the above conditions.[21] An unidentified intractable white solid residue (0.021 gm by difference) remained in the reaction tube.

(5) With methyl mercaptan

Methyl mercaptan (0.0342 gm; 0.713 mmole) was combined with IV (0.202 gm, 0.67 mmole) in a sealed tube and allowed to react at room temperature. After 30 minutes an unidentified bright yellow solid (0.044 gm by difference) was formed. Separation of the volatile products after one day of reaction gave $(CF_3)_2PS_2H$ (0.144 gm; 0.614 mmole), $(CF_3)_2PSH$ (0.006 gm; 0.03 mmole) and PF_3 (0.0426 gm; 0.483 mmole).

(6) With mercury

Triple distilled mercury (0.107 gm; 0.535 mmole) was added to IV (0.365 gm; 1.21 mmole) and shaken at room temperature for several days. The volatile products were $(CF_3)_4P_2S$ (0.213 gm; 0.576 mmole) and PF_3 (0.0293 gm; 0.288 mmole). A yellow solid residue in the reaction tube was found to contain $Hg[S_2P(CF_3)_2]_2$ (m/e (meas) 667.7861 (calc) 667.7877) and $Hg[S_2PF_2]_2$ (m/e (meas) 467.7989 (calc) 467.8002) by mass spectroscopy.

(7) With anhydrous methanol

IV (0.225 gm; 0.745 mmole) and CH_3OH (0.0245 gm; 0.765 mmole) were combined in a sealed tube. After 6 days reaction at room temperature, the volatile products were identified as $(CF_3)_2PS_2CH_3$ (0.156 gm; 0.63 mmole), a 6:1 mixture of $(CF_3)_2PS_2CH_3$ and $(CF_3)_2PS_2H$ (0.045 gm) (determined by nmr spectroscopy) and PF_3 (0.032 gm; 0.366 mmole). An unidentified solid residue remained in the reaction tube.

(8) With chlorine

To 0.253 gm (0.87 mmole) of IV was added 0.0516 gm (0.73 mmole) of Cl_2. This was allowed to react 24 hr at room temperature. No attempt was made to separate the product mixture but the entire volatile fraction was shown by ^{19}F nmr spectroscopy (mole % given in parentheses) to contain $(CF_3)_2P(S)SSP(S)(CF_3)_2$ (28%), $(CF_3)_2P(S)Cl$ (15%), $(CF_3)_2PCl$ (trace), $(CF_3)_2PCl_3$ (trace), PF_2Cl (52%), SPF_2Cl (4%) and PF_3Cl_2 (trace). No solid residues remained in the reaction vessel.

Reaction of $(CF_3)_2P(S)SP(CF_3)_2$ with dimethylamine

Anhydrous dimethylamine (0.0573 gm; 1.273 mmole) was combined with II (0.2558 gm; 0.636 mmole) in a sealed tube and allowed to warm to room temperature. Immediate reaction ensued with formation of a white solid identified by nmr

spectroscopy as $(CH_3)_2NH_2^+$ $(CF_3)_2PS_2^-$ (0.1687 gm; 0.605 mmole). The only volatile product was $(CF_3)_2PN(CH_3)_2$ (0.134 gm; 0.629 mmole).

Reactions of $F_2P(S)SPF_2$

(1) With anhydrous dimethylamine

Compound I (0.206 gm; 1.02 mmole) and dimethylamine (0.092 gm; 2.04 mmole) were combined and allowed to warm to room temperature. A white solid identified as $(CH_3)_2NH_2^+$ $F_2PS_2^-$ (0.1825 gm; 1.02 mmole) was formed immediately. The volatile products were $F_2P(S)N(CH_3)_2$, (0.002 g; 0.01 mmole), PF_3 (0.002 g; 0.04 mmole) and $F_2PN(CH_3)_2$ (0.103 gm; 0.91 mmole).

(2) With anhydrous methanol

Compound I (0.163 gm; 0.81 mmole) and methanol (0.0256 gm; 0.80 mmole) dried over sodium methoxide were allowed to react at room temperature for 4 hours. The volatile products (0.1699 gm) were determined by ^{19}F nmr spectroscopy to be $F_2P(S)SCH_3$ (73%), PF_3 (20%) and SPF_2SH (6%). A small amount of an involatile clear liquid (0.0186 gm by difference) which changed to a light yellow solid remained in the reaction tube and was not identified.

(3) With chlorine

Chlorine (0.0482 gm; 0.68 mmole) and I (0.1353 gm; 0.67 mmole) were allowed to react 15 hours at room tempera-

ture. The volatile products were found by ^{19}F nmr spectroscopy to be $F_2P(S)SSP(S)F_2$ (37%) and F_2PCl (63%). A small amount of involatile liquid which remained in the reaction tube was not identified.

(4) With methyl mercaptan

Methyl mercaptan (0.0266 gm; 0.55 mmole) and I (0.1143 gm; 0.57 mmole) reacted over 2 hours at room temperature to form an unidentified yellow solid, SPF_2SH (0.0428 gm; 0.32 mmole) and PF_3 (0.0434 gm; 0.49 mmole).

Preparation of difluorodithiophosphinic acid

SPF_2Cl (0.423 gm; 3.10 mmole), H_2S (0.014 gm; 3.12 mmole) and $(CH_3)_3N$ (0.368 gm; 6.24 mmole) were combined in a sealed tube. Immediate reaction ensued on warming to room temperature. After 12 hours the solid product was transferred to a round bottom flask. Addition of concentrated H_2SO_4 under vacuum liberated SPF_2SH (0.322 gm; 2.40 mmole) contaminated with a trace of SiF_4, and HCl (0.115 gm; 3.15 mmole) containing a small amount of SPF_2SH.

RESULTS AND DISCUSSION

(A) Synthesis of difluorothiophosphoryl-μ-thiobis(trifluoromethyl)phosphine ($F_2P(S)SP(CF_3)_2$) (III) and bis(trifluoromethyl)thiophosphoryl-μ-thiodifluorophosphine $(CF_3)_2P(S)SPF_2$ (IV).

The mixed substituent systems were prepared by analogy with the symmetrically substituted compounds using the general reaction

$$X_2PN(CH_3)_2 + 2Y_2PS_2H \longrightarrow X_2P\text{-}S\text{-}\overset{\overset{\large S}{\|}}{P}Y_2 + Y_2PS_2^-(CH_3)_2NH_2^+ \quad (5)$$

$(X,Y = F,\ CF_3)$ III : $X = CF_3$ $Y = F$
IV : $X = F$ $Y = CF_3$

These reactions are nearly quantitative and best yields were obtained when nearly stoichiometric quantities of reactants were used because of the difficulty of separating the product from reactants. Nmr spectroscopy at ordinary temperatures (Table I) confirms the existence of tri- and pentavalent phosphorus atoms in the molecules in agreement with previous results.[21,22]

The acid F_2PS_2H was conveniently prepared by the reaction of difluorothiophosphoryl chloride with hydrogen sulfide and trimethylamine to give the trimethylammonium salt of the acid:

$$SPF_2Cl + H_2S + 2(CH_3)_3N \longrightarrow (CH_3)_3NH^+\ F_2PS_2^- + (CH_3)_3NH^+Cl^- \quad (6)$$

TABLE 1

Coupling and Chemical Shift Parameters of Mixed Valence Compounds

	$F_2P(S)SP(CF_3)_2$ (III)	$(CF_3)_2P(S)SPF_2$ (IV)	$F_2P(S)SPF_2$ (I) (penta)	(tri)	$(CF_3)_2P(S)SP(CF_3)_2$ (II) (penta)	(tri)
$^1J_{FP}$	1223	1331	1209.9	1323.6	-	-
$^2J_{FP}$	78	113	-	-	111.7	81.3
$^3J_{FP}$	> 2[d]	18[d]	14.3	22.5	-	-
$^4J_{FP}$	n.o.[a]	1.8	-	-	4.9	0.6
$^4J_{FF}$	-	-	5.9,0	5.9,0	-	-
$^5J_{FF}$	0.7	n.o.[a]	-	-	-	-
$^6J_{FF}$	-	-	-	-	1.5	0.5
$^2J_{PP}$	96.5	73	67.8	67.8	103.0	103.0
ϕ_F^{III} b	55.0	61.2	-	60.8	-	53.8
ϕ_F^{IV} b	17.9	71.2	14.4	-	68.7	-
ϕ_P^{III} c	107.2	81.4	-	78	-	106.0
ϕ_P^{V} c	42.1	80.5	38.2	-	65.2	-

[a] coupling not observed

b ^{19}F shift from $CFCl_3$

c ^{31}P shift from P_4O_6

[d] coupling not completely resolved

The dithiophosphinic acid and hydrogen chloride are easily liberated from the salt mixture by reaction with concentrated sulfuric acid.

(B) Chemical reactions of the mixed valence compounds

As demonstrated in previous studies [21,22,39], reaction of the mixed valence compounds with protic species occurs preferentially at the P^{III}-S bond to form trivalent phosphines, X_2PZ, and dithiophosphinato acid or salts. The products are however greatly influenced by the stability of the phosphino product particularly in the case of difluorophosphino compounds of low stability.

Anhydrous hydrogen chloride reacted cleanly according to eq 7.

$$X_2P\text{-}S\text{-}\overset{\overset{\displaystyle S}{\|}}{P}Y_2 + HZ \longrightarrow X_2PZ + Y_2PS_2H \qquad (7)$$

with either $(CF_3)_2PCl$ or F_2PCl being recovered in expected amounts. Dimethylamine behaves similarly yielding stable amino phosphines $(CH_3)_2NPF_2$ or $(CH_3)_2NP(CF_3)_2$ plus the dimethylamino salt of the appropriate acid expected from eq 8.

$$Y_2PS_2H + R_2NH \longrightarrow R_2NH_2^+ + S_2PY_2^- \qquad (8)$$

Methyl mercaptan appears to react in a similar fashion since III gave $(CF_3)_2PSCH_3$ [40,41] and $F_2P(S)SH$ [23,42] however IV gave only $(CF_3)_2PS_2H$ [10,18], PF_3 and a bright yellow solid. The expected product, F_2PSCH_3, which has recently

been prepared and characterized [43], was not observed and may be unstable under the present reaction conditions. Similar behaviour was observed with I.[21] Methanol reacts with III to produce a very complex mixture of products, the main constituents of which were $(CF_3)_2PSH$ and $(CF_3)_2POCH_3$ in the ratio 4:3. Of the remaining 8 to 10 products contained in the mixture, only S_2PF_2H could be identified with certainty. The isomer IV reacts with methanol yielding only $(CF_3)_2P(S)SCH_3$ [18] and PF_3 plus a small amount of unidentified involatile material. These products can be explained as the result of a P^{III}-S cleavage by methanol following eq 7 to give $(CF_3)_2P(S)SH$ and F_2POCH_3. Decomposition or rearrangement of the latter would likely yield PF_3 whereas the former reacts <u>in situ</u> with methanol to give $(CF_3)_2P(S)SCH_3$ as demonstrated by a separate experiment:

$$(CF_3)_2P(S)SH + CH_3OH \longrightarrow (CF_3)_2P(S)SCH_3 + H_2O \qquad (9)$$

No water was detected amongst the reaction products since this will likely be consumed in the decomposition via hydrolyses of the fluorophosphine products.

Both compounds III and IV react readily with metallic mercury forming the dithiophosphinato complexes [44]

$$X_2P\text{-}S\text{-}\overset{\overset{\displaystyle S}{\|}}{P}Y_2 + Hg \longrightarrow [X_2P]_2 + Hg[S_2PY_2]_2 \qquad (10)$$

with the stable trifluoromethyl diphosphine $(CF_3)_4P_2$ result-

ing from III. The fluoro diphosphine F_2PPF_2 [35] expected from IV is unstable and decomposes to PF_3. One mole of PF_3 is expected in place of one mole of P_2F_4 [35] in agreement with the observed yield. The volatile products from IV also include $[(CF_3)_2P]_2S$ which presumably arises from the reaction of $(CF_3)_2P(S)-S-P(CF_3)_2$ (formed by exchange _vide infra_) with Hg:[22]

$$Hg + (CF_3)_2P(S)S-P(CF_3)_2 \longrightarrow HgS + [(CF_3)_2P]_2S \tag{11}$$

The solid product of the reaction of mercury was a mixture of $Hg[S_2P(CF_3)_2]_2$, expected by analogy with the behaviour of III with mercury and the unexpected difluorodithiophosphinate $[F_2PS_2]_2Hg$ which, according to the mass spectrum of the solid mixture, was present in relatively large quantities. Again the most likely source of the fluoro compound is the formation of $F_2P(S)-S-P(CF_3)_2$ by a rapid exchange mechanism (_vide infra_) which is faster in the case of IV compared to III and hence plays a more important role.

Chlorine reacts vigorously with III and IV with preferential cleavage at the P^{III}-S bond as well as oxidation of P^{III} to P^{V} species. Compound III yields $(CF_3)_2PCl$, $(CF_3)_2PCl_3$, a species which is probably $(SPF_2)_2S_2$ [38] (but which may be a higher polysulfide although this is unlikely) and SPF_2Cl. The latter is found in small amounts

only and may be due to scission of the P^V-S bond, or the decomposition of SPF_2SCl (which would result from P^{III}-S bond scission) or from the reaction of Cl_2 with one of the initial products of the reaction, eg $(SPF_2)_2S$.[37,38] $(CF_3)_2PCl_3$ formation is readily explained by addition of chlorine to the initially formed $(CF_3)_2PCl$. Compound IV gave $[(CH_3)_2P(S)]_2S_2$ [22] and F_2PCl as major products indicating scission of P^{III}-S to form either $(CF_3)_2P(S)SCl$ or $(CF_3)_2PS_2$ radicals which couple to form the tetrasulfide. A radical mechanism is the most likely precursor of this product. In addition, oxidation by Cl_2 occurs and $(CF_3)_2P(S)Cl$ [10] is found possibly as a result of abstraction of sulfur from $(CF_3)_2PS_2$ radicals or possibly some minor amount of attack on the P^V-S bond in the original compound.

Further characterization of the new compounds was achieved by alkaline hydrolysis. Compound III yielded 2 molar equivalents of CF_3H per mole of III whereas IV yielded only one. These stoichiometries are in agreement with those expected from the hydrolysis of $(CF_3)_2P^{III}$ and $(CF_3)_2P^V$ species.[13,45]

(C) Nmr spectra of III and IV

The room temperature nmr spectra together with the chemical results previously discussed confirm the existence of the mixed valence structure of compounds III and IV. In

III, the large fluorine-phosphorus coupling, $^{1}J_{FP}$ is 1223 Hz while the trifluoromethyl-phosphorus interaction, $^{2}J_{FP}$, is 78 Hz. These values are typical for one and two bond fluorine couplings to phosphorus in the penta- and trivalent oxidation states respectively. Similarly in compound IV, $^{1}J_{FP}$ is 1331 Hz and $^{2}J_{FP}$ is 113 Hz in keeping with the proposed structure.[16] Table 1 summarizes the nmr parameters obtained for the new compounds as well as those observed for the known mixed valence compounds I and II.

The trifluoromethyl region of the ^{19}F nmr spectrum of III shows what is apparently a five bond CF_3-F coupling of about 1 Hz which splits the major lines into asymmetric triplets. This asymmetry was also observed in I [21] and may be due to *cis* and *trans* couplings or to virtual coupling.[14] It seems odd that there is no observable interaction of the trifluoromethyl groups in compound III with the pentavalent phosphorus atom in either the ^{19}F or ^{31}P spectra. The ^{19}F spectrum of the fluorine atoms bound to P^{V} in compound III consists of the large doublet due to $^{1}J_{FP}$ and a further poorly resolved splitting of approximately 1 Hz forming apparent septets presumably due to coupling to the CF_3 groups on P^{III}. No interaction with P^{III}, $^{3}J_{FP}$, is observed at room temperature. The phosphorus nmr spectrum of III consists of an overlapping doublet of septets for P^{III} due to coupling to the two CF_3 groups and to P^{V}. The spectrum of P^{V} is a triplet of doublets from $^{1}J_{PF}$ and $^{2}J_{PP}$. The

spectra of some samples showed a very small amount of fine structure in the P^{III} region at room temperature which must be due to a small unresolved coupling to F on P^{V}.

As the temperature was lowered, all parts of the fluorine spectrum lost the fine structure arising from $^{5}J_{FF}$ and this coupling was never again resolved even at the low temperature limit of the spectrometer. At -120°C the CF_3 region of the spectrum consisted of only a doublet due to $^{2}J_{FP}$ and no interaction with P^{V} or F on P^{V} was observed. In some samples, the spectrum arising from the fluorine atoms on P^{V} had just passed coalescence at -120°C and were beginning to show doublet structure due to coupling with P^{III}. This coupling was never completely resolved, however, and its magnitude is uncertain although it is greater than 2 Hz. The ^{31}P nmr spectrum of the pentavalent phosphorus atom never showed any changes as the temperature was lowered and apparently P^{V} does not couple to CF_3 on P^{III}. The spectrum of P^{III} showed the fine structure observed at room temperature which sharpened slightly on lowering the temperature and appears as asymmetric triplets presumably due to $^{3}J_{FP}$. It is not clear why this coupling is not observed in the ^{19}F spectrum but perhaps overlap of lines resulting from $^{3}J_{FP}$ and $^{5}J_{FF}$ and non-observance of the very weak outer lines of the resultant multiplet tend to obscure $^{3}J_{FP}$.

The ^{19}F nmr spectra of IV at room temperature show no

couplings other than $^{1}J_{FP}$ and $^{2}J_{FP}$ in most samples although occasionally some samples showed $^{3}J_{FP}$ at this temperature. All samples on cooling gave rise to $^{3}J_{FP}$ of about 18 Hz but the temperature at which this coupling was resolved varied from sample to sample. In no case was $^{4}J_{FP}$, the coupling from CF_3 to P^{III}, observed in the ^{19}F nmr spectra nor was $^{5}J_{FF}$ ever seen. The ^{19}F spectra of all regions were quite broad at low temperatures and may have contained this information as unresolved splittings.

Two major differences in the nmr spectral behaviour of III and IV were noted. While the spectra of III were generally reproducible from sample to sample with the exception of very small coupling constants such as $^{3}J_{FP}$ which appeared at varying temperatures, it was extremely difficult to obtain reproducible spectra of IV. The other difference lay in the temperature at which $^{2}J_{PP}$ could be observed. In III, this coupling was always well resolved at room temperature whereas most samples of IV did not show this coupling at all until the temperature was decreased. In only one sample (Figure 2) was this interaction observed at room temperature and in this case the temperature was only slightly below that required for coalescence. The ^{31}P spectra at -40°C in this case consist of a doublet of septets of triplets for P^{V} due to $^{2}J_{PF}$, $^{2}J_{PP}$ and $^{3}J_{PF}$. The spectral region assigned to P^{III} shows a triplet of doublets of septets from $^{1}J_{PF}$, $^{2}J_{PP}$, and $^{4}J_{PF}$. Attempts to observe

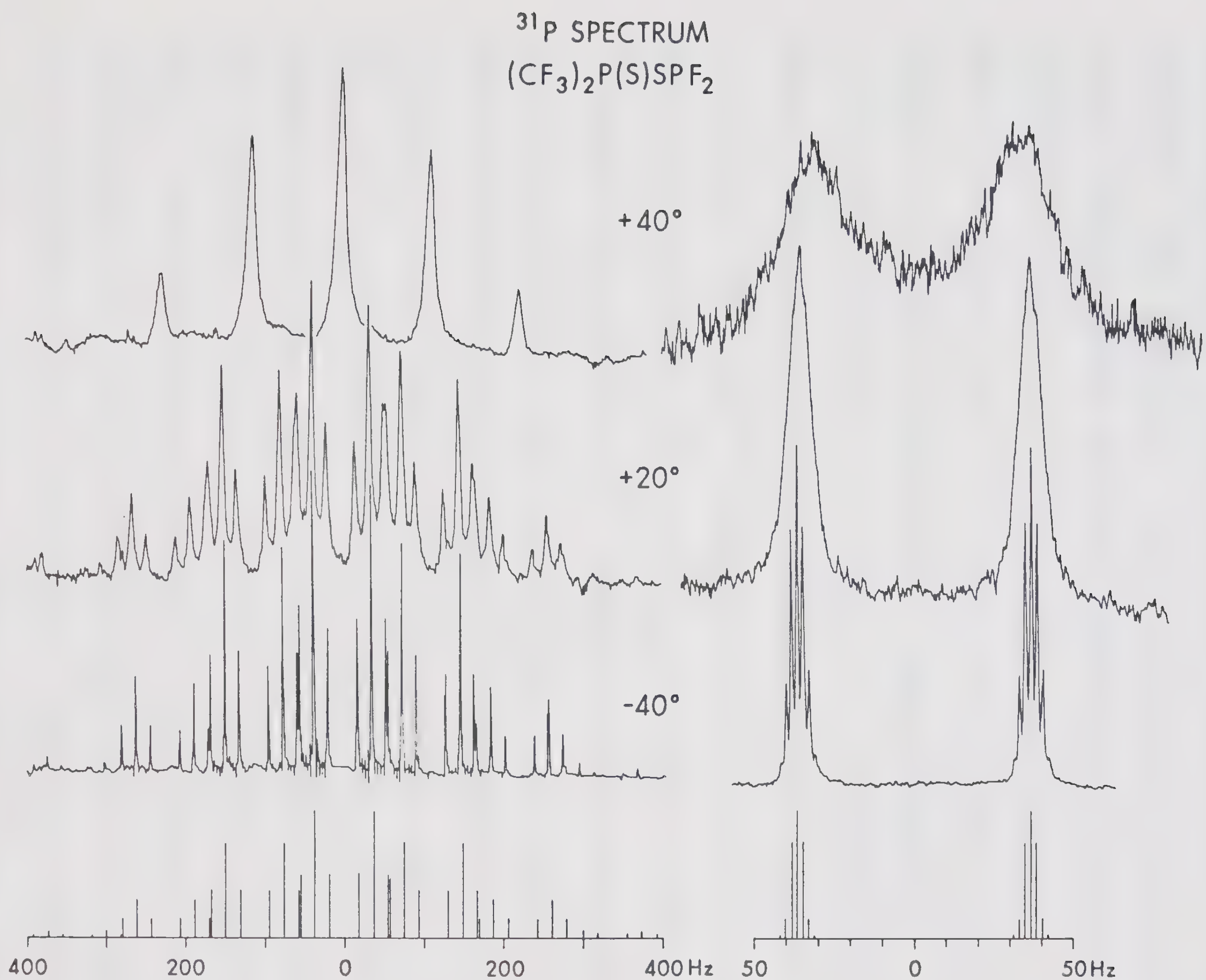
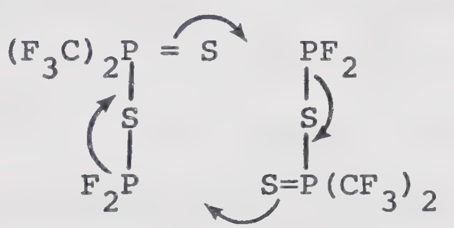


FIGURE 2. ^{31}P temperature dependent nmr spectrum of $(CF_3)_2P(S)SPF_2$ in CF_2Cl_2 solvent and the calculated first order pattern in the absence of exchange.

these couplings in this sample 24 hours later were unsuccessful and $^4J_{PF}$ was not observed although the sample had been maintained at liquid nitrogen temperatures in the interim. This behaviour led us to consider the possibility of an intermolecular exchange process as a mechanism for spectral averaging in the mixed valence compounds. This type of exchange could be catalysed by small amounts of impurities from decomposition of these compounds. If such an effect is important, then the nmr spectra should be concentration dependent and this was found to be the case in compound IV. The ^{31}P spectrum of a 29 mole % solution of III in CF_2Cl_2 did not show $^2J_{PP}$ or $^3J_{PF}$ at +40°C in the P^V region although the P^{III} region is just below its coalescence temperature for $^2J_{PP}$ at this temperature. (The origin of the different coalescence temperatures is discussed in greater detail below). By cooling this sample to 20°C $^3J_{FP}$ and $^2J_{PP}$ appeared in the P^V region but the P^{III} region did not show $^4J_{FP}$. By further cooling to -40°C all couplings were well resolved. A 1 mole % sample in CF_2Cl_2 from the same preparation of IV displayed all of these couplings at +40°C although they were not particularly well resolved at this temperature. Good resolution of all couplings was obtained, however, by 20°C for this sample. This behaviour supports the postulate of an intermolecular mechanism since a higher concentration is expected to yield a higher exchange rate and hence a more

poorly resolved spectrum. A similar study on compound III did not yield similar results but as was previously noted, the ^{31}P spectra of this compound did not show the high degree of temperature dependence that those of IV did.

A reasonable though not unique exchange process which satisfies the requirement that substituents do not suffer exchange from tri- to pentavalent phosphorus and hence do not show averaged couplings between different valencies is the bimolecular process involving an intermediate association of 2 molecules assuming terminal sulfur atoms to act as Lewis bases donating to acidic trivalent atoms:



The terminal sulfur atoms become bridging atoms and vice versa as the result of exchange of electron pairs whereas the phosphorus maintains a unique valence state. An equivalent polymeric process can of course be postulated which is compatible with the above bimolecular one. The present results exclude only monomolecular processes as a mechanism of exchange. A similar process can explain the equilibration results described below and is presumably responsible for the exchange process in $F_2P(S)SPF_2$ which was speculated to be a unimolecular process in the absence

of concentration studies.[21] The rate of exchange clearly varies with the substituents involved; hence it is reasonable to expect the present two compounds to be intermediate in behaviour to the rapid exchange observed in $F_2P(S)SPF_2$, where cooling to low temperatures was required to observe long range coupling [21], and the slow rate of exchange observed in $(CF_3)_2P(S)SP(CF_3)_2$, where all long range couplings are observed at room temperature.[22] It appears then that introduction of CF_3 substituents reduces the rate of exchange either through reduction of the Lewis acidity of the P^{III} centre or through some other influence on the formation of the intermediate associated complex and the electron transfer mechanism proposed. Another possibility is that greater chemical instability of the fluorosubstituted systems results in greater concentrations of catalytic impurities in the fluorosubstituted samples.

The appearance of the effects of P-P coupling on the P^{III} nmr lines at a higher temperature than that required for emergence of P-P coupling in the pentavalent phosphorus, nmr is also compatible with the above bimolecular exchange mechanism. In a typical exchange, a pentavalent phosphorus atom becomes coupled to a new $-PF_2$ unit and may "see" this unit in the spin states shown in Table 2(a). The spectral lines arising from transitions among these spin states are well separated since the P-F coupling ($^3J_{PF}$ = 18 Hz) is

TABLE 2

Nmr Spin States of Exchanging Species

(a)

P^{III}	F_2	f_i
α	$\alpha\alpha$	0.125
α	$\alpha\beta,\beta\alpha$	0.25
α	$\beta\beta$	0.125
β	$\alpha\alpha$	0.125
β	$\alpha\beta,\beta\alpha$	0.25
β	$\beta\beta$	0.125

(b)

P^{V}	$(CF_3)_2$	f_i
α	all combinations	0.5
β	all combinations	0.5

large. The fraction of exchanges leading to coupling of P^V to a $-PF_2$ unit in each of the respective spin states is designated f_i. A trivalent phosphorus atom encounters a similar situation but "sees" a new $(CF_3)_2P^V$ unit on exchange. In this case there are 14 different spin states available. However, since $^4J_{FP}$ = 1.8 Hz and $^2J_{P-P}$ = 73 Hz, the splitting of the lines due to the interaction of the trifluoromethyl fluorines and the phosphorus can be neglected and the P^{III} spectrum viewed approximately as arising from the two possible spin states of the P^V nucleus. Table 2(b) shows the spin states and the fraction of exchanges leading to them. Thus in a series of exchanges a pentavalent phosphorus atom is coupled to a new $-PF_2$ group in a different spin state (and hence gives rise to a different spectral line) in 7 of 8 exchanges. In contrast a trivalent phosphorus atom is coupled to a group of distinguishable $(CF_3)_2P$ spin states in only 4 of 8 exchanges. The pentavalent phosphorus therefore appears to have a faster chemical exchange rate than a trivalent one and a greater apparent reduction in rate is necessary to achieve the same spectral resolution of the P-P coupling.

To demonstrate the feasibility of the above postulate, equation 12, derived from the modified Bloch equations,[45] was used to calculate the theoretical lineshapes for the two phosphorus nuclei at various exchange rates. The spectral intensity $I(\omega)$ at frequency ω is given by

$$I(\omega) = \mathrm{Im} \quad -i\vec{f}(\underset{\sim}{D}-i\underset{\sim}{\Delta\omega})^{-1} \cdot \vec{1} \quad , \tag{12}$$

where

$$D_{ij} = \begin{cases} \dfrac{1}{\tau_i} - \dfrac{1}{T_{2i}} & i = j \\ P_{ij}/\tau_i & i \neq j , \end{cases} \tag{13}$$

$$\Delta\omega_{ij} = \begin{cases} \omega_{oi} - \omega & i = j \\ 0 & i \neq j , \end{cases} \tag{14}$$

$$1/\tau_i = (1-f_i)k \quad , \tag{15}$$

ω_{oi} is the frequency of the ith line in the absence of exchange, T_{2i} is the transverse relaxation time, P_{ij} is the probability of an exchange from state i to state j, and k is the rate constant for exchange in sec^{-1}.

Figure 3 shows the results of these calculations at various rates of exchange k. It can be seen that at a rate of 250 sec^{-1}, the P^{III} spectrum shows more resolution than P^{V} spectrum, although the difference is not as pronounced as in the observed spectra (see Figure 2). From this model, it would appear that P^{III} is exchanging at a rate of 150 or 200 sec^{-1} and P^{V} at 300 or 400 sec^{-1}. This is clearly impossible but it will be noted that the exchange rate varies from about 500 to 0.001 sec^{-1} in the temperature interval +40 to +20°C; a factor of 5×10^5. Thus very small variations in temperature may account for the discrepancy since

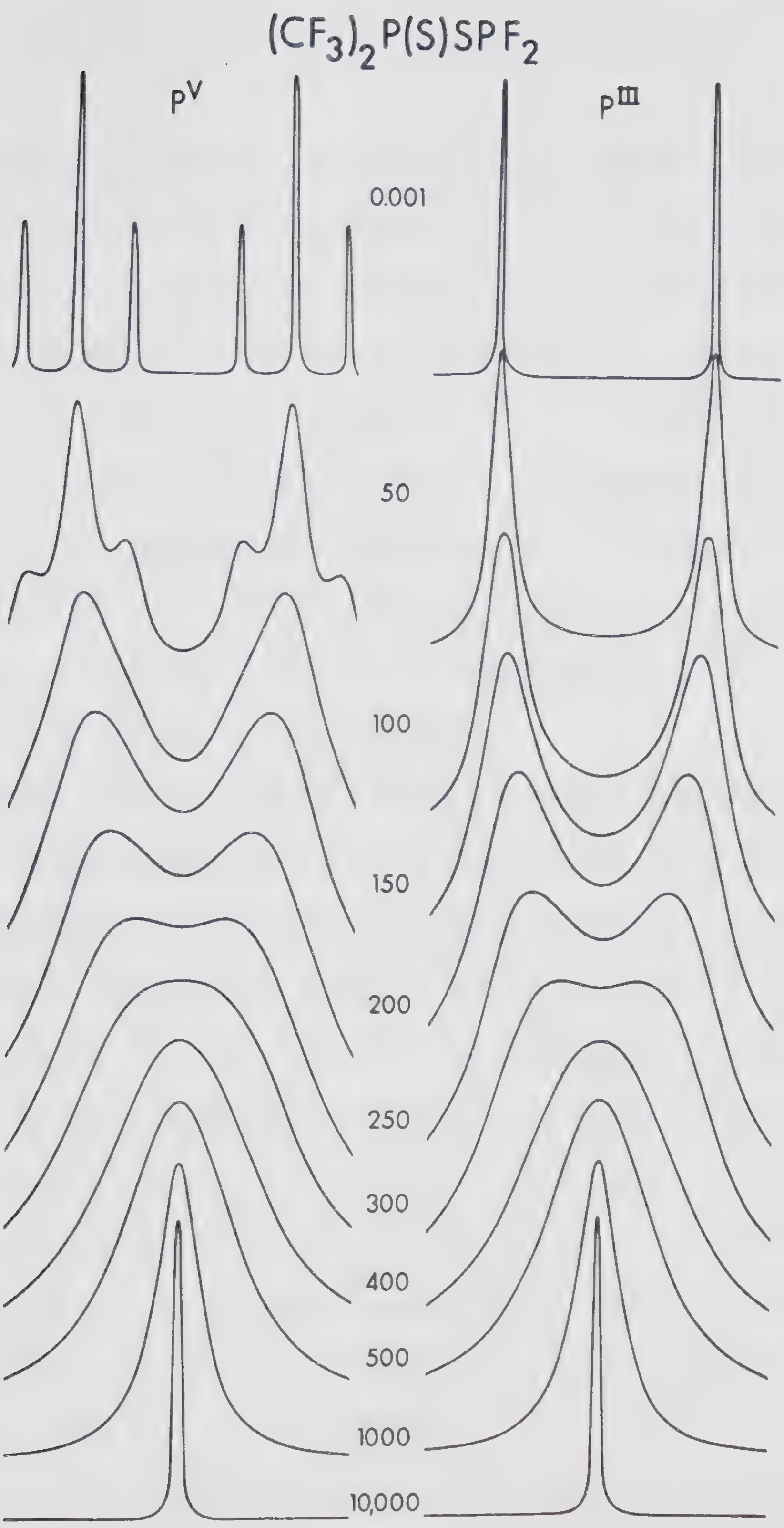


FIGURE 3. Theoretical lineshapes of the ^{31}P spectra of $(CF_3)_2P(S)SPF_2$ at exchange rates varying from 0.001 to 10,000 sec^{-1}.

the P^{III} and P^{V} spectra were observed separately.

D. <u>Molecular exchange phenomena and thermal stability</u>

The difficulty experienced in obtaining reproducible temperature dependent nmr spectra led us to consider in more detail the possible mechanism of molecular exchange and to determine in particular whether inter- or intra-molecular exchange were more likely sources. Concentration dependent nmr studies, although not unambiguous did suggest that intermolecular processes were important and we accordingly investigated the possibility of exchange of P^{III} and P^{V} fragments with unique substituents.

Mixing III and IV in $CFCl_3$ solution produced an immediate reaction with initial formation of a white solid which quickly dissolved on shaking. Immediate analysis of the constitution of the mixture by ^{19}F nmr spectroscopy showed the presence of all four mixed valence compounds I, II, III and IV. Assignments, and normalized integrated proportions are given in Table 3. Low temperature spectra of the mixture resulted in resolution of long range coupling not observed at room temperature which serves to confirm the assignments. A small change in relative proportions of the species was also observed.

From normalized integrated intensities the equilibrium constant for the reaction

TABLE 3

Chemical Exchange of Mixed Valence Compounds

	ϕ (ppm)[a]	J_{FP} (Hz)[a]	III + IV at 40°C integral[b]	III + IV at -80°C integral[b]	I + II at 40°C integral[b]
I(tri)	60.8	1324	23[c]	144	25[c]
I(penta)	14.4	1210	27	123	19
II(tri)	53.8	81.3	25	160	9
II(penta)	68.7	111.7	27	147	9
III(tri)	55.0	79	25	117	13
III(penta)	17.9	1225	27	115	16
IV(tri)	61.2	1331	17[c]	78	15[c]
IV(penta)	71.2	113	20	83	11
K			1.6 ± 0.7	2.1 ± 0.7	1.1 ± 0.7

a ϕ and J from pure room temperature samples $^{1}J_{FP}$ for directly bound fluorine, $^{2}J_{FP}$ for trifluoromethyl.

b integrals normalized to 2 fluorines per phosphorus

c peaks overlap - intensities from ratios of other end of the molecule

$$(CF_3)_2P\text{-}S\text{-}P(S)F_2 + F_2PS\text{-}P(S)(CF_3)_2 \rightleftharpoons F_2P(S)SPF_2 + (CF_3)_2P(S)SP(CF_3)_2 \quad (16)$$

III IV I II

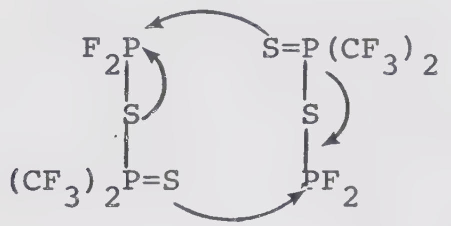
was obtained:

$$K = \frac{[I][II]}{[III][IV]} = 1.6 \pm 0.7\ (40°C),\ 2.1 \pm 0.7\ (-80°C)$$

The reaction (as written) is exothermic by no more than 500 cal and considering the accuracy of K, is probably more nearly thermoneutral. The reverse reaction was demonstrated by mixing equal proportions of I and II which equilibrated at room temperature to give K (as defined above) of 1.1 at 40°C. These data are also included in Table 3. This labile equilibration is notable in that it does not involve a change in the valence state of phosphorus. The process suggested above to explain the nmr exchange behaviour is compatible with the chemical exchange noted herein.

The mixed valence compounds (I, II, III, IV) have different thermal stability with II being the most stable of all of the compounds.[22] Heating III to 200° for prolonged periods yielded negligible decomposition, whereas IV deposited a white solid even at room temperature. Nmr analysis of the products of decomposition of IV at 70° showed a mixture

of II, III, IV and PF_3. Compound I may also have been present and have escaped detection because of its low concentration and small fluorine content, but it is more likely that it decomposes to PF_3 [21] under the conditions of the reaction. It seems likely that the least stable compounds of the system, I and IV, (i.e. the compounds with trivalent PF_2 groups) undergo a second exchange mechanism which can permit mutual oxidation-reduction of phosphorus resulting in apparent interchange of substituents.



This second mechanism reflects the greater ease with which fluorine substituted phosphorus (III), as compared to trifluoromethyl P^{III}, is oxidized to P^{V}, and is not unexpected in view of the relative stabilities of P^{III} vs P^{V} with F and CF_3 substituents. It is likely that the rate of this process is slower than the facile interchange observed in the nmr spectra since it involves more electronic reorganization with a consequently greater activation energy and of course it can only be observed when different substituents provide labels on the phosphorus atoms.

CHAPTER 4

MIXED VALENCE COMPOUNDS WITH ASYMMETRIC PHOSPHORUS CENTRES

INTRODUCTION

Compounds of phosphorus in the trivalent oxidation state with both trifluoromethyl groups and fluorine atoms attached have been known for some time. These include such species as CF_3PF_2 [47], $CF_3P(F)Cl$ [48], $CF_3P(F)N(CH_3)_2$ [48] and $(CF_3)_2PF$.[16] The first and last of these are conveniently made from the corresponding iodo phosphine and antimony trifluoride while $CF_3P(F)N(CH_3)_2$ is obtained from the reaction of stoichiometric amounts of CF_3PF_2 and dimethylamine. Although $CF_3P(F)Cl$ is known to disproportionate on standing [48] it was formed when $CF_3P(F)N(CH_3)_2$ and HCl were reacted. Several pentavalent phosphorus anions with these groupings are also known including such species as $(CF_3)_3PF_3^-$ [49], $(CF_3)_2PF_4^-$ [49], $CF_3PF_5^-$ [49], $(CF_3)_2PF_3H^-$ [50] and $CF_3PF_4H^-$ [50,51] which are analogous to the well known hexafluorophosphate anion, PF_6^-. Perhaps the most extensively studied series of compounds containing both CF_3 and F bound to phosphorus are the five coordinate trifluoromethylfluoro phosphoranes.[52,53] Although extensively investigated by spectroscopic techniques [52b], investigations continue [53] because there are several unresolved problems concerning the symmetry of these molecules. Only very few phosphoryl and thiophosphoryl species with this substitution have been

prepared these being $CF_3P(O)F_2$ [54], $CF_3(F)P(S)N(CH_3)_2$ [10], $(CF_3)_2P(S)F$ [10], and $(CF_3)_2P(O)F$.[55] This Chapter reports the synthesis of $CF_3P(S)F_2$ and the new dithiophosphinic acid $CF_3(F)PS_2H$, its dimethylammonium salt, and some mixed valence compounds derived from it.

Members of the series $CF_3(F)P(S)S-X$ (X = $(CF_3)_2P-$, F_2P-, $CF_3(F)P-$) and $CF_3(F)P-X$ (X = $(CF_3)_2PS_2-$, F_2PS_2-, $CF_3(F)PS_2-$) were found to be rather interesting molecules since in the first series the pentavalent phosphorus and in the latter the trivalent one are located in asymmetric environments, thus making the molecules optically active. Burg and his coworkers have recently synthesized several compounds containing both a methyl and a trifluoromethyl group attached to trivalent phosphorus.[56-58] These include $CF_3(CH_3)PCl$, $CF_3(CH_3)PI$, $CF_3(CH_3)PNH_2$, $CF_3(CH_3)PN(H)CH_3$ and the diphosphorus compounds $(CF_3(CH_3)P)_2$ [56], and $(CF_3(CH_3)P)_2S$.[58] The diphosphorus compounds were found to exist as two isomers whose nmr spectra, although similar, were chemically shifted from one another. It is postulated that these isomers arise from an asymmetric environment about phosphorus which leads to a racemic mixture of d and l forms and the meso compound.[57] Optical isomerism can only be observed if the trivalent phosphorus atom either cannot invert or does so at a slow rate on the nmr time scale. As has been shown previously, phosphorus has a much higher barrier to inversion than does nitrogen [59] and Burg has found

that even at 200°C spectral coalescence in the ^{19}F nmr spectrum of $(CF_3(CH_3)P)_2$, which would result from rapid phosphorus inversion, does not occur.[57] As well, the separability of optical isomers of trivalent phosphorus has been demonstrated elsewhere.[60]

It has been shown that in $(i\text{-}C_3H_7)_2NP(Cl)C_6H_5$, the methyl groups within the isopropyl groupings are chemically non-equivalent in the nmr due to the asymmetry or chirality [61] of the phosphorus atom. This non-equivalence is independent of internal rotations of the molecule.[62] In this Chapter, use is made of chiral phosphorus in both the trivalent and pentavalent oxidation states to measure geminal CF_3-CF_3 and F-F nmr coupling constants. As well the compound $CF_3(F)P(S)SP(F)CF_3$, which has two optically active phosphorus centres, has been shown by nmr to exist as a mixture of two racemates.

EXPERIMENTAL

Fluorotrifluoromethyldithiophosphinic Acid

1. Reactions of $CF_3(F)PN(CH_3)_2$

(a) With H_2S

A mixture of $CF_3(F)PN(CH_3)_2$ (0.1436 gm; 0.88 mmole) and H_2S (0.0624 gm; 1.83 mmole) was heated for 60 hr at 70°C and for an additional 6 hr at 100°C. The volatile products (0.0374 gm) were removed and found by mass spectroscopy to contain CF_3PH_2 and H_2S. A solid residue was left in the tube (see below).

(b) With HI

To $CF_3(F)PN(CH_3)_2$ (0.1906 gm; 1.17 mmole) was added HI (0.3000 gm, 2.34 mmole). Immediate reaction ensued on warming to room temperature with evolution of elemental iodine. The volatile products are mainly CF_3PI_2 and CF_3PF_2 in the ratio 3:2 contaminated with a trace of CF_3PH_2. The solid residue was found to contain the dimethylammonium cation with only a trace of an unidentified fluorine containing species.

(c) With sulfur

$CF_3(F)PN(CH_3)_2$ (0.6635 gm; 4.07 mmole) was heated at 150°C for 3 days with an excess of sulfur. Fractionation of the volatile products at -45°C yielded a mixture (0.3102 gm) of $CF_3(F)P(S)N(CH_3)_2$, $CF_3P(S)(N(CH_3)_2)_2$ and two other

unidentified products in much smaller amounts. The -96°C trap contained $CF_3(F)P(S)N(CH_3)_2$ (0.2409 gm) contaminated with about 5% of $F_2P(S)N(CH_3)_2$ while the -196°C fraction was pure $CF_3P(S)F_2$ (0.1629 gm).

2. Reactions of the solid residue from $CF_3(F)PN(CH_3)_2$ + H_2S

(a) With anhydrous HCl

To the solid residue (0.1676 gm by difference) was added anhydrous HCl (0.0686 gm; 1.88 mmole). This was allowed to react 16 hr at 30°C. The volatile products were fractionated and found to contain HCl contaminated with another unidentified product (0.0766 gm). A solid remained in the reaction tube. To this solid was added F_2PS_2H (0.1404 gm; 1.05 mmole) which was allowed to react for 2½ hr at 30°C. Fractionation of the volatile products yielded HCl (0.0182 gm; 0.50 mmole) and F_2PS_2H (0.0716 gm; 0.54 mmole). A white oily liquid remaining in the reaction tube was dissolved in CD_3CN. The nmr spectrum of this solution indicated the main constituent of the oily liquid to be $(CH_3)_2NH_2^+$ $F_2PS_2^-$ contaminated with small amounts of $CF_3PO_2H^-$ and $CF_3PSO_2H^-$.

(b) With bromine

The solid residue (0.2294 gm by difference) was reacted with bromine (0.0842 gm; 0.53 mmole) for 1 hr at 25°C.

The volatiles were removed (0.0360 gm) leaving an intractable solid in the reaction tube.

(c) Nmr spectroscopic studies of the solid residue

The solid residue (0.1452 gm) was dissolved in CD_3CN and sealed in an nmr tube. The ^1H nmr showed the presence only of the dimethylammonium cation. The ^{19}F nmr indicated $CF_3P(H)O_2^-$ as well as several unidentified fluoro-phosphorus compounds. After 2 days at room temperature a white solid had precipitated from the solution.

3. Reactions of $CF_3(F)P(S)N(CH_3)_2$

(a) With HI

$CF_3(F)P(S)N(CH_3)_2$ (0.2213 gm; 1.13 mmole) was mixed in an evacuated glass tube with HI (0.438 gm; 3.42 mmole). Immediate reaction on warming to room temperature was observed with formation of a red liquid. The tube was allowed to stand for 60 hr at 30°C by which time elemental iodine was deposited on the walls of the vessel. The volatile fraction (0.2315 gm) consisted mainly of CF_3PI_2 and $CF_3P(S)F_2$ contaminated with small amounts of several other unidentified compounds one of them probably being $CF_3P(H)I$ ($^2J_{FP}$ = 56 Hz, $^3J_{FH}$ = 10 Hz, ϕ_F = 50.7 ppm). The solid residue was found to contain the dimethylammonium cation (by nmr) but contained no fluorine bound to phosphorus.

(b) With H_2S

$CF_3(F)P(S)N(CH_3)_2$ (0.1663 gm; 0.55 mmole) and H_2S (0.0301 gm; 0.89 mmole) were mixed in a sealed tube and placed in an oven at 170°C for 4 days. The volatile products were removed and found to contain H_2S (0.0171 gm; 0.50 mmole) and unreacted $CF_3(F)P(S)N(CH_3)_2$ (0.0807 gm; 0.41 mmole). An oily liquid which remained in the tube was dissolved under a nitrogen atmosphere in dry CD_3CN. The nmr spectrum of the sample showed the presence of $(CH_3)_2NH_2^+ F_2PS_2^-$ and $(CH_3)_2NH_2^+ CF_3(F)PS_2^-$ ($^1J_{FP}$ = 1071 Hz, $^2J_{FP}$ = 103 Hz, $^3J_{FF}$ = 1 Hz; ϕ_F = 37.4 ppm; ϕ_{CF_3} = 77.8 ppm) inthe approximate ratio 1:2.

4. Reaction of $CF_3(F)PS_2^-$ with H_2SO_4

To approximately 2.14 mmoles of $(CH_3)_2NH_2^+CF_3(F)PS_2^-$ contaminated with $F_2PS_2^-$ $(CH_3)_2NH_2^+$ was added a large excess of concentrated H_2SO_4 under vacuum. An immediate reaction ensued with liberation of volatile products (0.3338 gm). The ^{19}F nmr spectrum indicated the presence of a mixture F_2PS_2H (27.5%) and $CF_3(F)PS_2H$ (72.5%) which was found to be inseparable by fractionation. The vapor phase molecular weight of the mixture was 171.4. By assuming equal volatility of the two compounds and ideal gas behaviour a molecular weight of 185.5 (calc 184) for $CF_3(F)PS_2H$ is found. The parent ion of $CF_3(F)PS_2H$ was measured in the

mass spectrometer (meas. 183.9194, calc for CF_4PS_2H, 183.9194). The nmr spectrum was consistent with that which was expected for the new compound. The ^{19}F spectrum showed a doublet of doublets ($^2J_{FP}$ = 132 Hz; $^3J_{FF}$ = 3.1 Hz; ϕ_{CF_3} = 75.0 ppm) corresponding to a CF_3 group coupling to phosphorus and to a single fluorine atom and a doublet of quartets ($^1J_{FP}$ = 1169 Hz; $^3J_{FF}$ = 3.1 Hz; ϕ_F = 54.1 ppm) due to coupling of a fluorine nucleus to phosphorus and to a CF_3 group. The proton gave rise to a singlet centred at τ 6.67 in the ^1H nmr spectrum. The ir spectrum recorded using a reference cell containing F_2PS_2H (<u>vide</u> <u>infra</u>) was consistent with that expected for $CF_3(F)P_2SH$. (2600 w; 2580 vw; ν_{SH} : 1190 vs,br; ν_{CF} : 910 s, 830 m,br; ν_{PF}, δ_{SH} : 765 m, 725 s; δ_{sym,CF_3}, $\nu_{P=S}$: 570 s, 535 m, 415 m; δ_{as,CF_3}, ν_{PS}, ν_{PC}). The amount of F_2PS_2H present as impurity varied from one preparation to another.

5. Preparation of $CF_3P(S)F_2$

An excess of elemental sulfur and CF_3PF_2 (0.2373 gm; 1.72 mmole) were heated at 150°C for 2 days. The very volatile products were not separable but nmr analysis indicated a mixture of unreacted CF_3PF_2 (86%) and $CF_3P(S)F_2$ (14%). Reaction of CF_3PF_2 (0.2171 gm; 1.57 mmole) with excess sulfur for 14 days at 170°C gave $CF_3P(S)F_2$ in 100% yield. The vapor phase molecular weight was 167 (calc 170).

6. Preparation of $CF_3(F)P(S)SP(CF_3)_2$ (V)

A sample of $CF_3(F)PS_2H$ contaminated with F_2PS_2H (0.1848 gm; 1.004 mmole based on $CF_3(F)PS_2H$) was added to $(CF_3)_2PN(CH_3)_2$ (0.1182 gm; 0.555 mmole). Fractionation of the products yielded $CF_3(F)P(S)SP(CF_3)_2$ (0.1574 gm; 0.448 mmole) which was contaminated with $F_2P(S)SP(CF_3)_2$ and $CF_3(F)PS_2H$. An oily involatile liquid formed in the reaction was identified by nmr spectroscopy as $(CH_3)_2NH_2^+$ $CF_3(F)PS_2^-$ contaminated with $(CH_3)_2NH_2^+$ $F_2PS_2^-$.

7. Reactions of $CF_3(F)P(S)SP(CF_3)_2$

(a) With $(CH_3)_2NH$

A sample of $CF_3(F)P(S)SP(CF_3)_2$ from the previous preparation (0.0854 gm; 0.242 mmole) reacted immediately at room temperature with $(CH_3)_2NH$ (0.0244 gm; 0.54 mmole) to yield $(CF_3)_2PN(CH_3)_2$ (0.0502 gm; 0.235 mmole) as the only volatile product.

(b) Alkaline hydrolysis

Reaction of V (0.0690 gm; 0.196 mmole) with a 20% aqueous solution of NaOH yielded fluoroform (0.0232 gm; 0.332 mmole) as the only volatile product.

8. Preparation of $CF_3(F)P(S)SPF_2$ (VI)

A sample of $CF_3(F)PS_2H$ (0.2930 gm; 1.59 mmole) contaminated by a small amount of F_2PS_2H and a trace of SiF_4 reacted immediately on warming to room temperature with

$F_2PN(CH_3)_2$ (0.0905 gm; 0.80 mmole) with formation of a clear viscous liquid. The only volatile product was $CF_3(F)P(S)SPF_2$ (0.1755 gm; 0.697 mmole) contaminated with $F_2P(S)SPF_2$ which could not be removed. The viscous liquid reacted with concentrated H_2SO_4 to yield $CF_3(F)PS_2H$ (0.1279 gm; 0.695 mmole).

9. Reactions of $CF_3(F)P(S)SPF_2$

(a) With $(CH_3)_2NH$

A mixture of $CF_3(F)P(S)SPF_2$ (0.1131 gm; 0.45 mmole) and $(CH_3)_2NH$ (0.0414 gm; 0.82 mmole) reacted on warming to give $PF_2N(CH_3)_2$ (0.0355 gm; 0.314 mmole) and PF_3 (0.0109 gm; 0.124 mmole) and a yellowish solid (0.1007 gm) which reacted with concentrated H_2SO_4 to give $CF_3(F)PS_2H$ (0.0541 gm; 0.294 mmole) containing a small amount of F_2PS_2H.

(b) Alkaline hydrolysis

A sample of $CF_3(F)P(S)SPF_2$ (0.0604 gm; 0.240 mmole) reacted vigorously with a large excess of a 20% aqueous NaOH solution. No volatile products were detected.

10. Preparation of $(CF_3)_2P(S)SP(F)CF_3$ (VII)

A mixture of $(CF_3)_2PS_2H$ (0.4903 gm; 2.095 mmole) and $CF_3(F)PN(CH_3)_2$ (0.1784 gm; 1.10 mmole) reacted immediately on warming to room temperature with formation of a white solid identified by nmr spectroscopy as $(CF_3)_2PS_2^-$ $(CH_3)_2NH_2^+$. A volatile liquid which decomposed slowly during room temperature transfers in the vacuum

system was identified as $(CF_3)_2P(S)SP(F)CF_3$. The yield of product purified by fractionation and refluxing from a micro reflux column was 42% (0.1555 gm; 0.442 mmole).

11. Reactions of $(CF_3)_2P(S)SP(F)CF_3$

(a) With $(CH_3)_2NH$

A mixture of $(CF_3)_2P(S)SP(F)CF_3$ (0.0775 gm; 0.220 mmole) and $(CH_3)_2NH$ (0.0218 gm; 0.484 mmole) formed a white solid when warmed to 25°C. This was identified by nmr spectroscopy as $(CF_3)_2PS_2^-$ $(CH_3)_2NH_2^+$. The only volatile product was $CF_3(F)PN(CH_3)_2$ (0.0309 gm; 0.19 mmole) contaminated with a small amount of $(CH_3)_2NH$.

(b) Alkaline Hydrolysis

A sample of $(CF_3)_2P(S)SP(F)CF_3$ (0.0780 gm; 0.222 mmole) which slowly decomposed on transferring to the reaction vessel was combined with a 20% aqueous solution of NaOH. The only volatile product isolated was CF_3H (0.0271 gm; 0.388 mmole).

12. Preparation of $F_2P(S)SP(F)CF_3$ (VIII)

Warming a mixture of F_2PS_2H (0.7337 gm; 5.47 mmole) and $CF_3(F)PN(CH_3)_2$ (0.4455 gm; 2.73 mmole) to 25°C resulted in immediate formation of $F_2PS_2^-$ $(CH_3)_2NH_2^+$ (0.4502 gm; 2.52 mmole) which was identified by nmr spectroscopy. The lone volatile product was identified as $F_2P(S)SP(F)CF_3$ (0.5341 gm; 2.12 mmole).

13. Reactions of $F_2P(S)SP(F)CF_3$

(a) With $(CH_3)_2NH$

A pure sample of $F_2P(S)SP(F)CF_3$ (0.1709 gm; 0.678 mmole) reacted immediately at 25°C with $(CH_3)_2NH$ (0.0600 gm; 1.332 mmole) to form a white solid (0.1202 gm; 0.672 mmole) identified from its nmr spectrum as $F_2PS_2^-$ $(CH_3)_2NH_2^+$. The only volatile product was $CF_3(F)PN(CH_3)_2$ (0.1082 gm; 0.665 mmole).

(b) Alkaline hydrolysis

A sample of $F_2P(S)SP(F)CF_3$ (0.1480 gm; 0.588 mmole) was combined with an excess of a 20% aqueous solution of NaOH. The only volatile product was CF_3H (0.0393 gm; 0.562 mmole).

14. Preparation of $CF_3(F)P(S)SP(F)CF_3$ (IX and X)

A sample of $CF_3(F)PS_2H$ (0.1570 gm; 0.85 mmole) reacted immediately with $CF_3(F)PN(CH_3)_2$ (0.0764 gm; 0.47 mmole) with formation of a viscous oil which was identified as $CF_3(F)PS_2^-$ $(CH_3)_2NH_2^+$ contaminated with a small amount of $F_2PS_2^-$ $(CH_3)_2NH_2^+$ from its nmr spectrum. An undetermined amount of $CF_3(F)P(S)SP(F)CF_3$ which was identified from its nmr spectrum was obtained as the volatile product.

RESULTS

A. Synthesis and Chemistry of $CF_3(F)P(S)SH$ and related compounds.

The reaction of trifluoromethylfluorodimethylamino-phosphine $(CF_3)(F)PN(CH_3)_2$ with hydrogen sulfide was performed in an attempt to emulate the preparation of $(CF_3)_2PSH$ from $(CF_3)_2PN(CH_3)_2$.[63] The desired compound, $CF_3(F)PSH$ was not obtained, rather CF_3PH_2 [64] was the only volatile product and a solid residue remained. Attempts to obtain the nmr spectrum of the solid proved fruitless although precautions were taken to exclude air and moisture. The solid, which was only sparingly soluble in CD_3CN or CH_2Cl_2, showed proton signals attributable to the dimethylammonium cation, and in the case of the CD_3CN solution showed numerous very weak ^{19}F nmr signals, one set of which correspond to those expected from $CF_3P(H)O_2^-$.[19] The CH_2Cl_2 solution showed no ^{19}F nmr signals. After two days at room temperature, a white solid precipitated from the acetonitrile solution but not from the dichloromethane solution. The solid may be the analog of the product obtained from the reaction of SPF_2H and $(CH_3)_2NH$ which was formulated as the dimethylammonium salt of SPF_2^- ion.[65] This adduct is however unstable in solution and is not well characterized at the present time.

An attempt was made to prepare the trivalent acid, $CF_3(F)PSH$, by the reaction of the solid with HCl in the hope

that sulfur could be added to it to form the dithiophosphinic acid, $CF_3(F)P(S)SH$. An unidentified volatile product was obtained as a contaminant of the excess HCl and a solid remained in the reaction tube. Addition of F_2PS_2H [23] yielded only HCl, equivalent to that which had been consumed in the preceding step and excess F_2PS_2H. The solid remaining in the tube was shown by nmr spectroscopy to contain $(CH_3)_2NH_2^+$ $F_2PS_2^-$ as its main constituent as well as small amounts of $CF_3PO_2H^-$ [19] and $CF_3PSO_2H^-$ [19] ions. The solid was not completely soluble in the CD_3CN solvent.

Addition of slightly less than a calculated stoichiometric amount of bromine to the solid product yielded only a small amount of volatile products and an intractable solid, neither of which were identified. No diphosphorus disulfur compound was formed, as would have been expected if the reaction of $CF_3(F)PS^-$ had been similar to that of $(CF_3)_2PS_2^-$ which gave $(CF_3)_2P(S)SSP(S)(CF_3)_2$.[22]

From the preceding experiments, it is clear that identification and isolation of either $CF_3(F)PSH$ or a salt of the acid is difficult and provides no useful preparative routes.

The reaction of $CF_3(F)PN(CH_3)_2$ with HI yielded iodine, CF_3PI_2 and CF_3PH_2 as the only volatile products. These products can be accounted for assuming that the initial reaction of HI gave $CF_3P(F)I$ as expected which in turn is followed by subsequent halide exchanges forming the

two dihalophosphines. The presence of elemental iodine and CF_3PH_2 suggested that some reduction of the rearrangement products occurred as well. The solid remaining in the reaction tube contained the dimethylammonium cation and traces of fluorine containing species.

Addition of elemental sulfur to $CF_3(F)PN(CH_3)_2$ has previously been shown to be non-stoichiometric.[10] As well as the normal addition of sulfur to give $CF_3(F)P(S)N(CH_3)_2$, we have now also identified $CF_3P(S)(N(CH_3)_2)_2$ and $CF_3P(S)F_2$, which were presumably formed as rearrangement products of the desired compound. Surprisingly, varying amounts of $F_2P(S)N(CH_3)_2$ [66] were also identified as a component of the reaction products. This compound is very difficult to separate from the major component by conventional vacuum techniques and propagation down the synthetic routes (<u>vide infra</u>) to $CF_3(F)PS_2H$ and the mixed valence compounds gave no improvement in the ease of separation.

The impure $CF_3(F)P(S)N(CH_3)_2$ prepared by the foregoing method, was reacted with HI in an attempt to synthesize $CF_3(F)P(S)H$ by a reaction analogous to that used to prepare $F_2P(S)H$.[67] On warming to room temperature, an immediate reaction occurred to give a red liquid. After 2½ days at room temperature, during which time elemental iodine was deposited on the walls of the reaction vessel, the products were CF_3PI_2, $CF_3P(S)F_2$ and a compound whose nmr spectrum was consistent with that expected for $CF_3P(H)I$. The

$CF_3P(S)F_2$ presumably arises from HX cleavage of the P-N bond and subsequent disproportionation to form $CF_3P(S)F_2$ and perhaps $CF_3P(S)I_2$. This latter product may then be reduced to $CF_3P(SH)I$, (or $CF_3P(H)I$) and I_2 by HI. In the former case, further disproportionation and decomposition could give CF_3PI_2 and $CF_3P(H)I$. The dithiophosphinic acid salt $(CH_3)_2NH_2^+\ S_2P(F)CF_3^-$ which was the product of the reaction of $CF_3(F)P(S)N(CH_3)_2$ with H_2S had an nmr spectrum that agreed very well with the spectrum predicted empirically by comparison with those of $(CF_3)_2PS_2^-$ and $F_2PS_2^-$.[23] Unfortunately the $F_2P(S)N(CH_3)_2$ impurity in the starting material gave rise to considerably higher relative amounts of the difluoro acid salt, suggesting further disproportionation of $CF_3(F)P(S)N(CH_3)_2$. Reaction of the salts with concentrated H_2SO_4 under vacuum easily liberated $CF_3(F)PS_2H$ contaminated with F_2PS_2H. The new dithiophosphinic acid was identified from its nmr spectrum. The presence of the F_2PS_2H precludes clear identification by most other methods such as infrared spectroscopy. From the experimentally determined gas phase molecular weight of the mixture (171.4) and the mole fractions of the components (F_2PS_2H = 27.5%; $CF_3(F)PS_2H$ = 72.5%) as determined by nmr spectroscopy the molecular weight of the new compound was found to be 185.5 (calc for CHF_4PS_2 = 184). The infrared spectrum of $(CF_3)FP(S)SH$ was obtained by comparison of a sample cell containing the above mixture with a reference beam sample

cell containing pure F_2PS_2H. The spectrum so obtained is consistent with that expected for the new compound. Mass measurement of the parent ion in the mass spectrum confirmed the presence of $CF_3(F)PS_2H$ (see above).

B. Nmr studies of mixed valence compounds containing chiral centres.

To further characterize the new acid, the reaction with $(CF_3)_2PN(CH_3)_2$ was performed to give the new diphosphorus disulfur mixed valence compound $CF_3(F)P(S)SP(CF_3)_2$. This new compound, fluoro(trifluoromethyl)thiophosphoryl-μ-thio bis(trifluoromethyl)phosphine (V) which forms a new member of the series of mixed valence fluorophosphorus compounds $F_2P(S)SPF_2$ (I), $(CF_3)_2P(S)SP(CF_3)_2$ (II), $F_2P(S)SP(CF_3)_2$ (III), $(CF_3)_2P(S)SPF_2$ (IV), is of interest because it contains a chiral [61,62] phosphorus centre. Chirality in a four coordinate phosphorus compound can confer chemical non-equivalences in groups remote from the central phosphorus atom. In the present case, the four different species bound to the pentavalent phosphorus atom cause chemical non-equivalence of the two trifluoromethyl groups bound to the trivalent phosphorus, allowing a rare opportunity to observe directly a four bond CF_3-CF_3 coupling constant which has previously been observed only in the spectra of some five-coordinate phosphoranes.[52b] The Newman projections for the various rotamers of V are shown

in Figure 4. It is clear that internal rotations in the

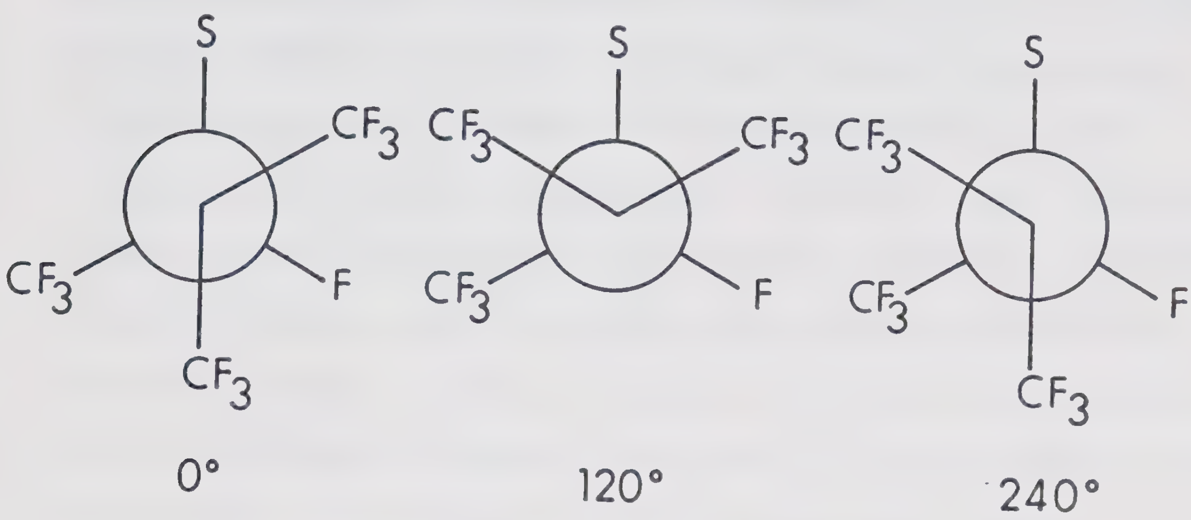


FIGURE 4. Newman projections of the rotamers of $CF_3(F)P(S)SP(CF_3)_2$ (V)

molecule do not destroy the non-equivalence of the two trifluoromethyl groups since they can never be exchanged one for the other by an intramolecular rotation. Thus they must always be in different magnetic environments, as must their averages. An inversion of the trivalent phosphorus atom would however allow exchange between these environments. Since our experiments show that there are always two unique CF_3 chemical shifts for CF_3 on P^{III} within the temperature range studied, it is concluded that phosphorus inversion occurs at a very slow rate in comparison to the time scale of the nmr experiment.[14] Three other new compounds $CF_3(F)P(S)SPF_2$ (VI), $(CF_3)_2P(S)SP(F)CF_3$ (VII) and $F_2P(S)SP(F)CF_3$ (VIII) have been found to exhibit similar non-

equivalences and their nmr spectra as well as that of V have been matched with spectra calculated using the computer program NUMAR [68] in order to extract chemical shift and coupling constant information especially from spectral regions which require second order analysis. This non-iterative program requires as input coupling constants, relative chemical shifts, and linewidths for transitions arising from the various nuclei. A best fit of the observed spectra is obtained by manual adjustment of estimations of these values and recalculation of the theoretical results.

The numbering scheme, which is used to specify the various nuclei to the program is given in the tables of nmr parameters obtained from these fitting procedures (see below), and does not imply a particular stereochemistry for the non-equivalent groups in these molecules. The graphic output of the program obtained on a CALCOMP plotter is shown under the observed spectra in diagrams presented in this Chapter as an indication of the success of the match.

1. <u>Fluoro(trifluoromethyl)thiophosphoryl-μ-thiobis(trifluoromethyl)phosphine (V)</u>

The ^{19}F and ^{31}P spectra of $CF_3(F)P(S)SP(CF_3)_2$ (V) are shown in Figure 5 and a complete tabulation of the nmr parameters obtained by the previously mentioned matching procedures are given in Table 4. The spectrum of the non-

FIGURE 5. Observed and calculated ^{19}F and ^{31}P nmr spectrum of $CF_3(F)P(S)SP(CF_3)_2$ (V) determined from a 30% v/v $CFCl_3$ solution. ^{19}F spectrum obtained at 40°C at 94.1 MHz with $CFCl_3$ as both lock and reference compound. Fourier transformed ^{31}P spectrum obtained at 40°C at 36.4 MHz with a $CFCl_3$ heteronuclear lock and an external P_4O_6 reference. Impurity lines marked by asterisks.

5(a) ^{19}F spectral region arising from CF_3 on P^{III}. Impurity lines due to CF_3 on P^{III} in $F_2P(S)SP(CF_3)_2$ (III).

5(b) ^{19}F spectral region of CF_3 on P^{V}.

5(c) ^{19}F spectral region of F on P^{V}.

5(d) P^{III} region of ^{31}P spectrum. Impurity lines due to P^{III} in $F_2P(S)SP(CF_3)_2$ (III).

5(e) Half of P^{V} region of ^{31}P spectrum. Impurity lines due to $CF_3(F)P(S)SH$.

^{19}F N.M.R. SPECTRUM

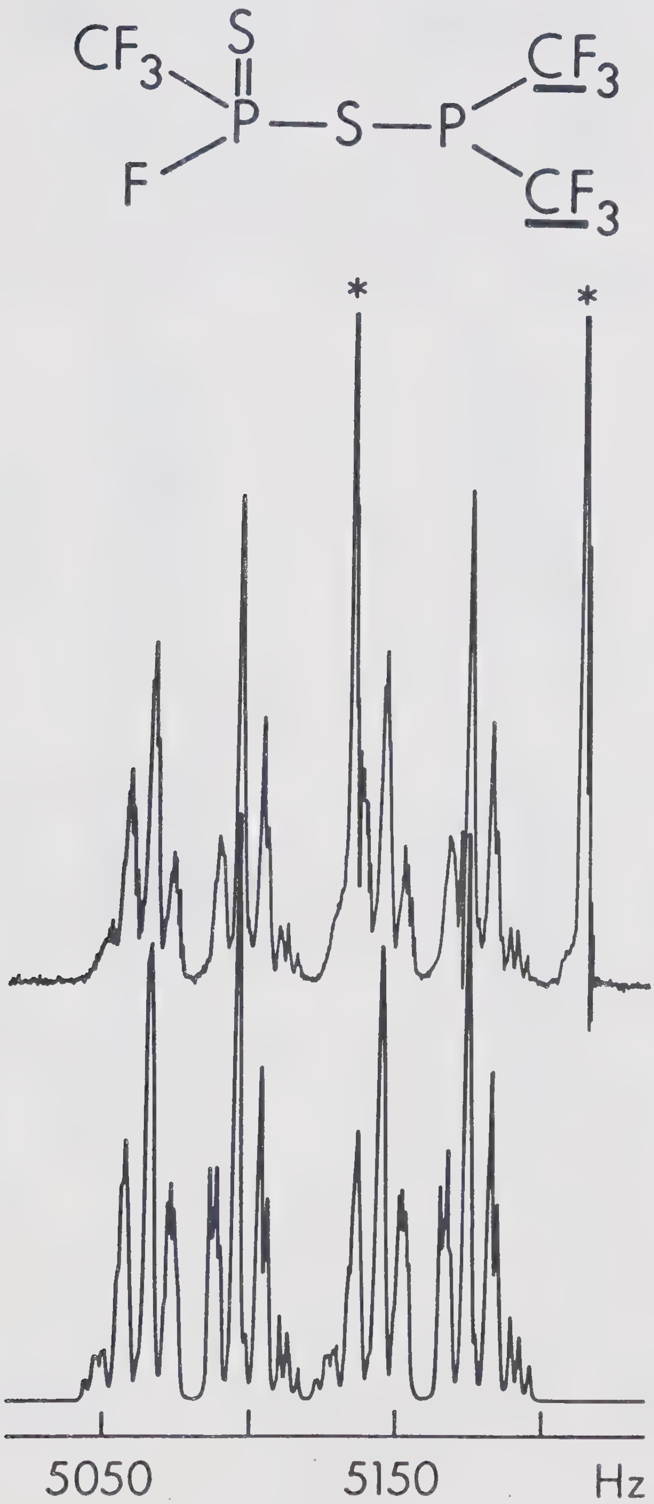


FIGURE 5a

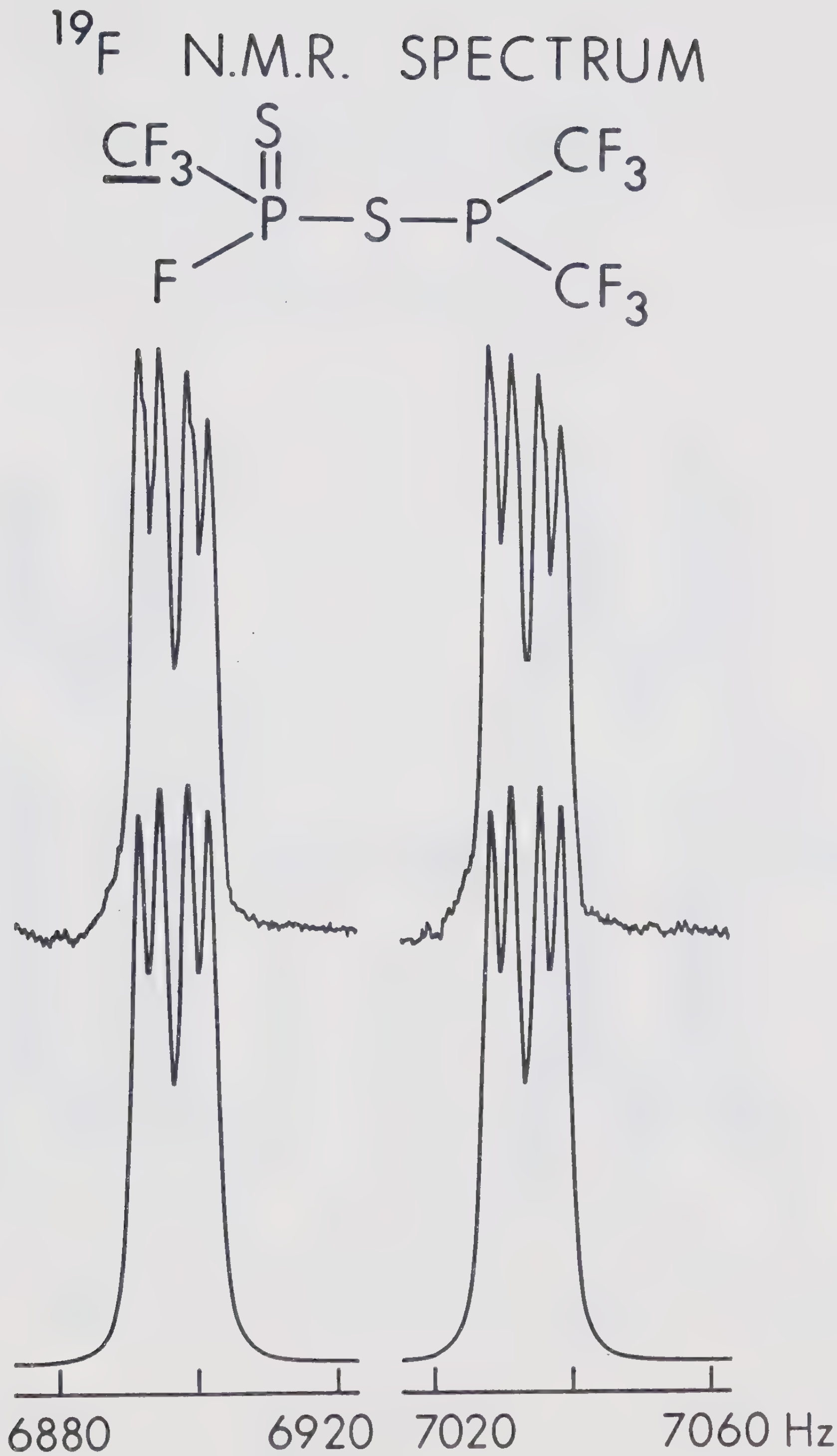
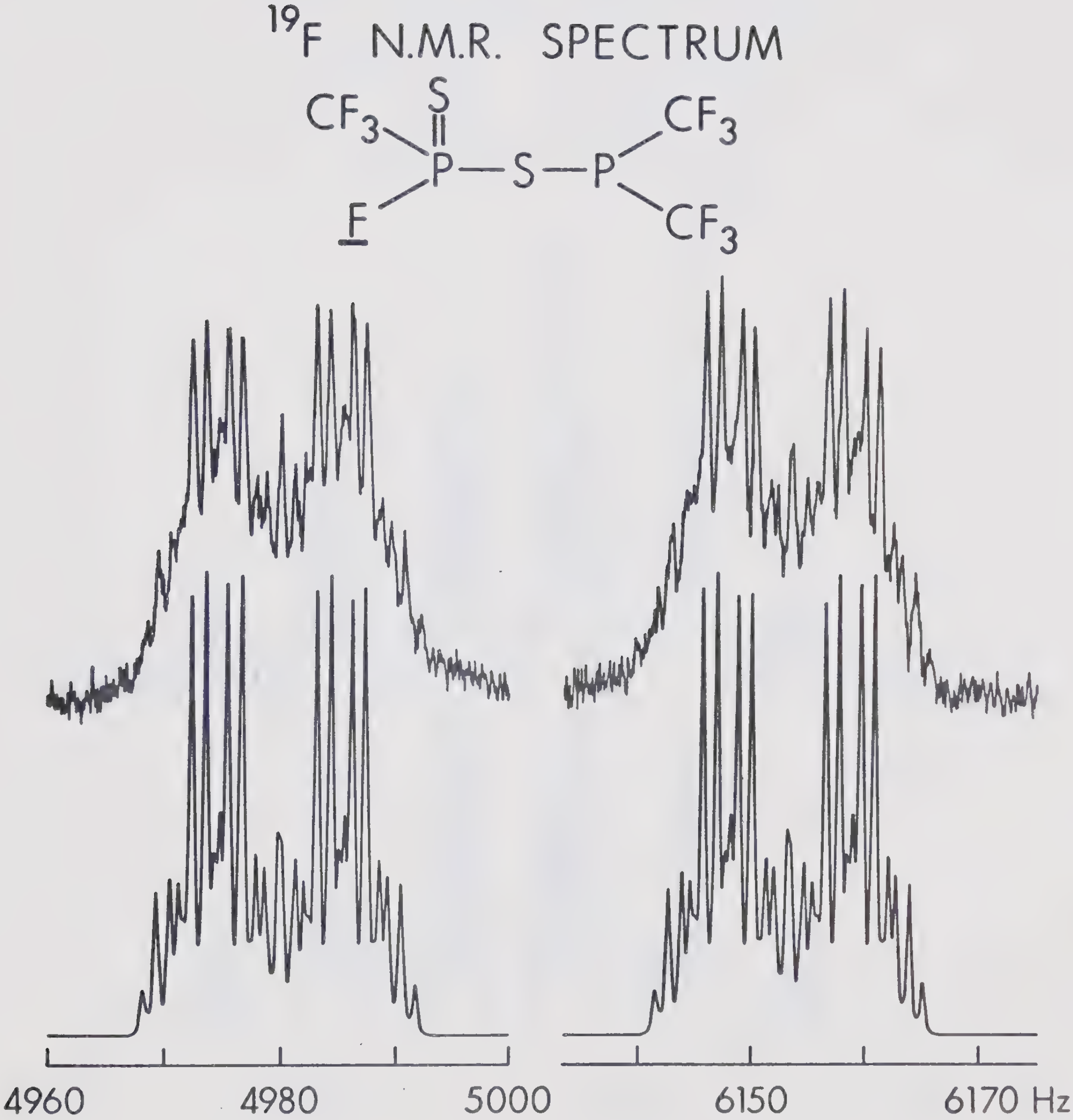


FIGURE 5b



^{19}F N.M.R. SPECTRUM
S
CF_3
P
S
P
CF_3
F
CF_3
4960
4980
5000
6150
6170 Hz

FIGURE 5c

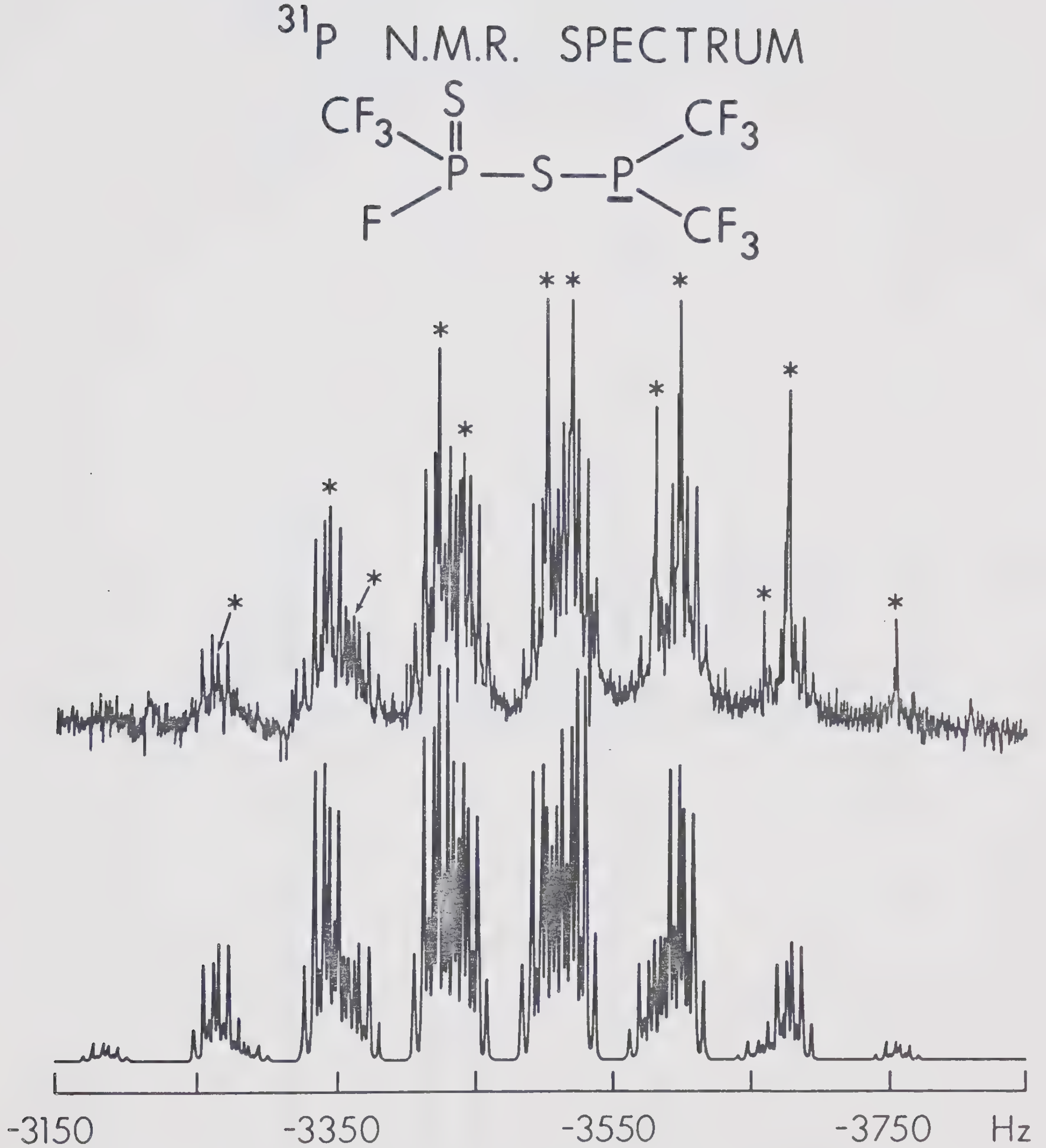


FIGURE 5d

^{31}P N.M.R. SPECTRUM

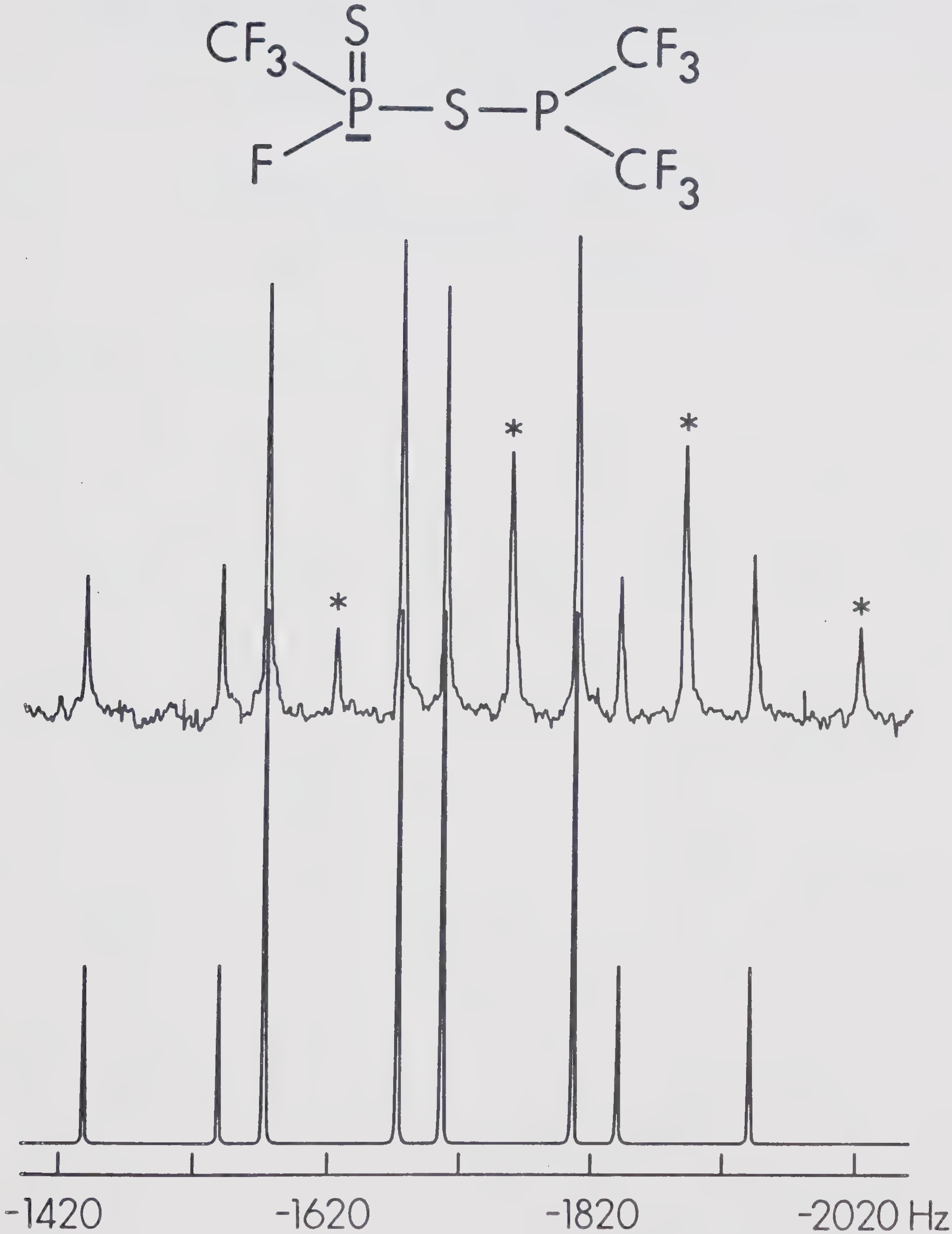
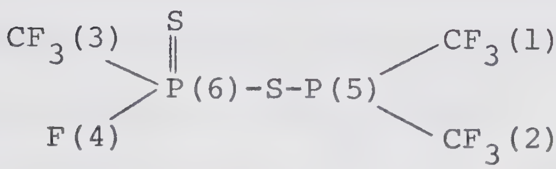


FIGURE 5e

TABLE 4

Nmr Coupling and Chemical Shift Parameters for

$CF_3(F)P(S)SP(CF_3)_2$ (V)



(V)

coupling constants (Hz)

1-2 = 9.0

1-3 = 0.0 2-3 = 0.0

1-4 = 1.2 2-4 = 0.0 3-4 = 3.0

1-5 = 78.5 2-5 = 78.5 3-5 = 7.0 4-5 = 10.5

1-6 = 0.0 2-6 = 0.0 3-6 = 134.5 4-6 = 1173.4 5-6 - 100.0

chemical shifts	linewidths (Hz)
ϕ_1 = 5100.3 Hz $(54.2)^a$ $(48.3)^c$	L_1 = 1.0
ϕ_2 = 5136.8 Hz $(54.5)^a$ $(48.5)^c$	L_2 = 1.0
ϕ_3 = 6962.8 Hz $(74.0)^a$ $(68.1)^c$	L_3 = 2.4
ϕ_4 = 5565.9 Hz $(59.2)^a$ $(53.3)^c$	L_4 = 0.4
ϕ_5 = -3562 Hz $(100.5)^b$	L_5 = 1.4
ϕ_6 = -1102 Hz $(34.8)^b$	L_6 = 1.0

a) shift from $CFCl_3$ (ppm) at 94.1 MHz

b) shift from P_4O_6 with $CFCl_3$ lock (ppm) at 36.4 MHz

c) shift from CF_2Cl_2 (ppm) at 94.1 MHz

equivalent trifluoromethyl groups bound to P^{III} (Figure 5a) is second order and may be analysed as an A_3B_3X system with first order couplings to the pentavalent end of the molecule. The lines indicated by asterisks are due to the CF_3 groups of the $F_2P(S)SP(CF_3)_2$ (III) impurity which results from the F_2PS_2H impurity in $CF_3(F)PS_2H$. The trifluoromethyl group bound to P(V) is seen to suffer first order coupling to P^V, P^{III} and the single fluorine nucleus on P^V (Figure 5b). The spectrum of the fluorine atom on P^V exhibits first order couplings to all other magnetic nuclei in the molecule except one of the non-equivalent CF_3 groups (Figure 5c). This region of the spectrum presents special problems in obtaining satisfactory matches between observed and calculated results since its features are determined by small differences between relatively large couplings and small changes in the magnitude of these interactions can create rather major alterations in the appearance of the calculated spectrum. It is seen however that satisfactory agreement between observed and calculated spectra has been achieved.

The nmr spectrum of the trivalent phosphorus atom (Figure 5d) presents the same difficulties in achieving satisfactory fits as does that of the fluorine atom bound to P^V but it too is analysed on the basis of first-order interactions. The main features of this spectral region consist of an overlapping doublet of septets due to coupling to P^V

and to the two CF_3 groups to which it is bound. Further coupling to the groupings on P^V results in rather complicated fine structure since each of the major lines is now split into a doublet of quartets. Lines marked with an asterisk arise from transitions of the trivalent phosphorus atom in the $F_2P(S)SP(CF_3)_2$ impurity. The nmr spectrum of P^V (Figure 5e) consists of a large doublet from coupling to the single fluorine atom, which is further split into a quartet of doublets due to interaction with the CF_3 group bound to it and with P^{III}. No coupling to the non-equivalent CF_3 groups is observed. Although the ^{31}P spectrum of $CF_3(F)PS_2H$ has not been measured, the F-P couplings observed in the quartet impurity lines in this region of the spectrum are consistent with what would be expected for $CF_3(F)PS_2H$.

2. <u>Fluoro(trifluoromethyl)thiophosphoryl-μ-thiodifluro-phosphine (VI).</u>

The nmr spectra of $CF_3(F)P(S)SPF_2$, a compound in which chirality of P^V renders the two fluorine atoms on P^{III} non-equivalent, are presented in Figure 6 and Table 5 gives the nmr parameters which were derived from these spectra. The main difficulty in calculating theoretical spectra for this molecule was to assign the major resonances in the fluorine region. The CF_3 group spectral lines are easily recognized and form a doublet of doublets due

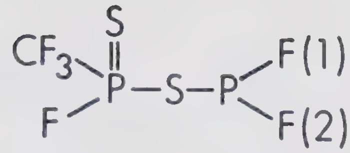
FIGURE 6. Observed and calculated ^{19}F and ^{31}P nmr spectrum of $CF_3(F)P(S)SPF_2$ (VI) determined from a 30% v/v CF_2Cl_2 solution. ^{19}F spectrum obtained at -120°C at 94.1 MHz with CF_2Cl_2 as both lock and reference compound. Fourier transformed ^{31}P spectrum obtained at 36.4 MHz at -120°C with CF_2Cl_2 as heternuclear lock compound and P_4O_6 as external reference. Impurity lines marked by asterisks.

6(a) ^{19}F spectral region due to CF_3 on P^V.

6(b) ^{19}F spectral region arising from F on P^V and F on P^{III}.

6(c) ^{31}P spectrum of P^{III}. Impurity lines due to P^{III} in $F_2P(S)SPF_2$ (I).

6(d) Half of ^{31}P spectrum due to P^V. Impurity lines not identified.

^{19}F SPECTRUM OF 

CF_3 on P^V

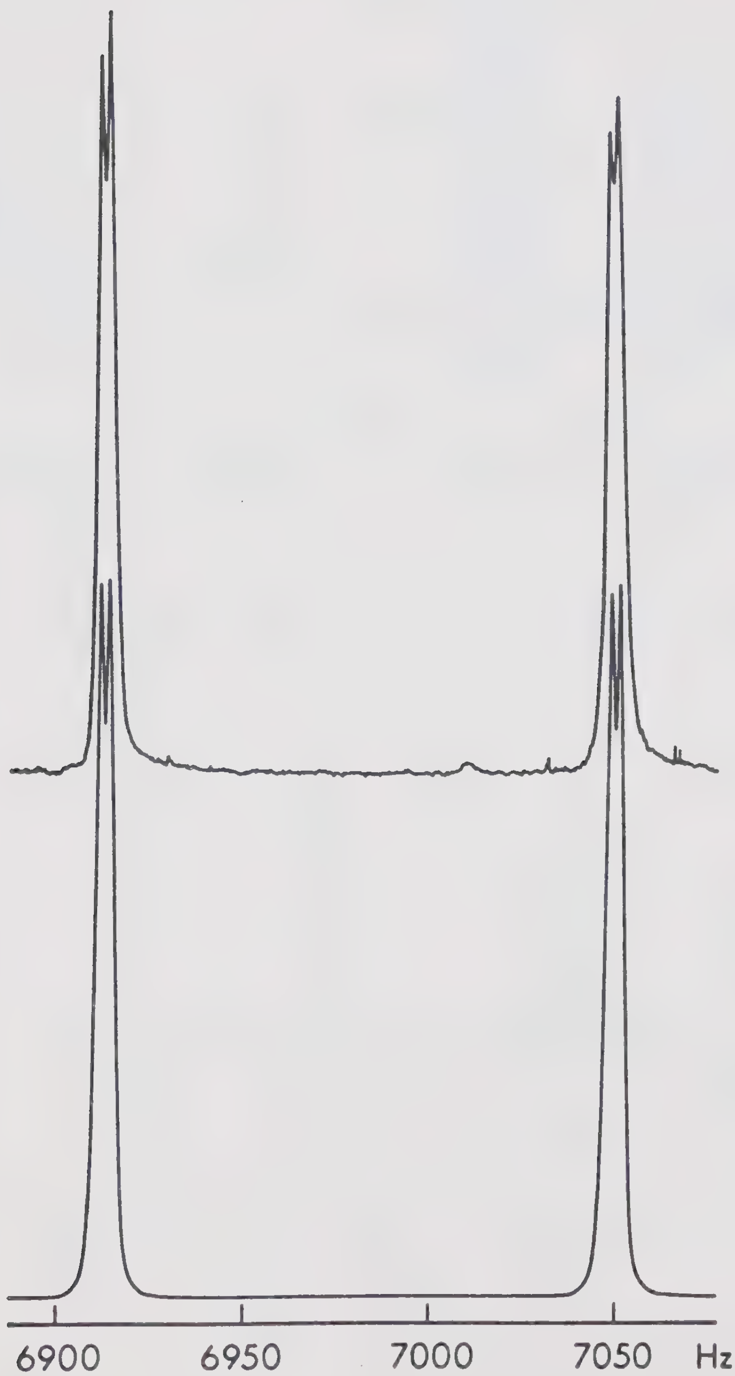


FIGURE 6a

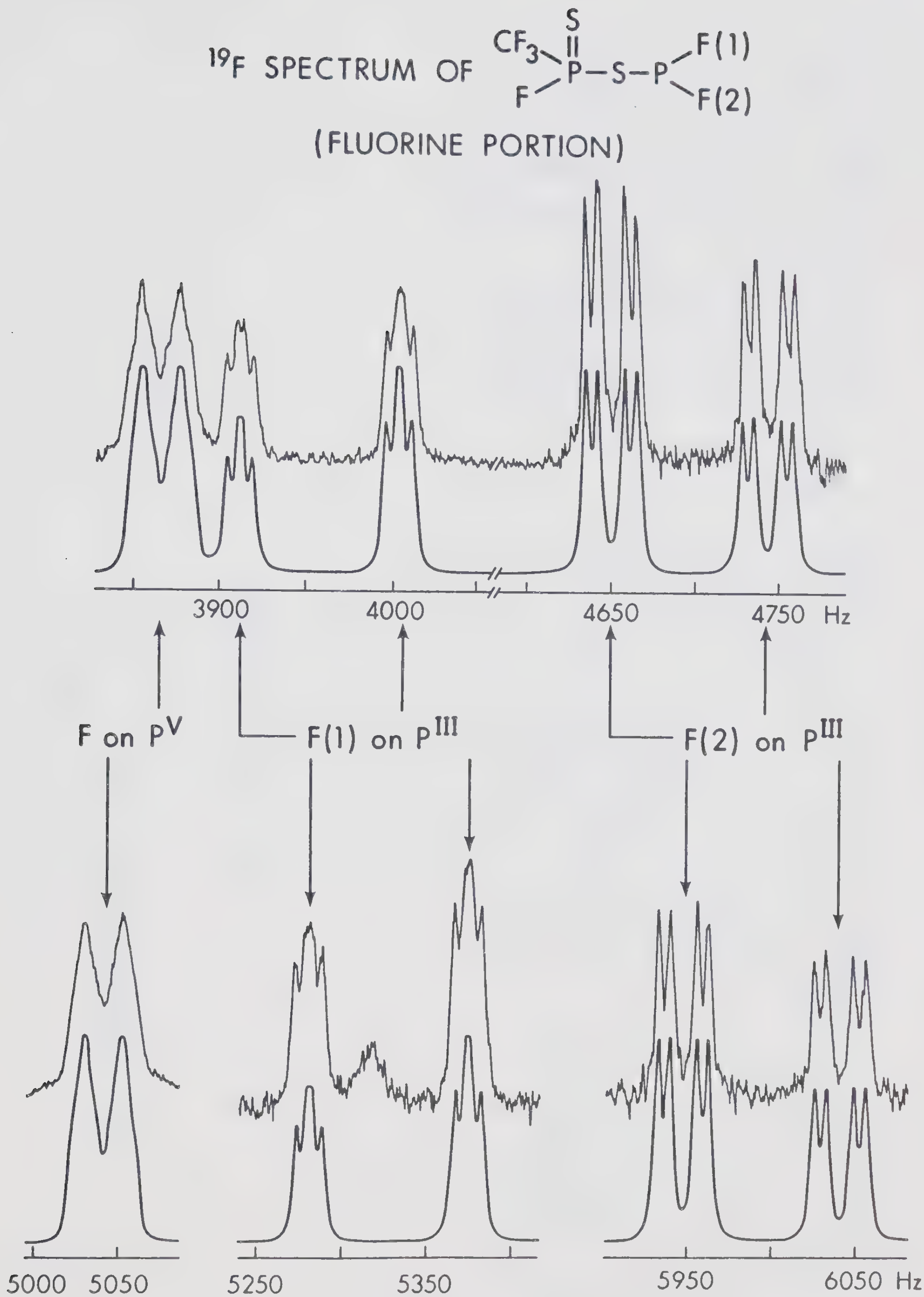
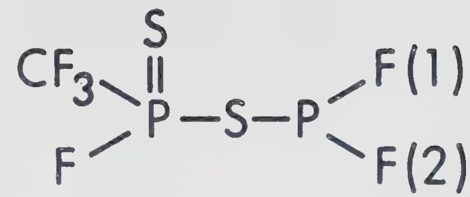

19F SPECTRUM OF
S
CF3
P—S—P
F
F(1)
F(2)
(FLUORINE PORTION)
3900
4000
4650
4750 Hz
F on PV
F(1) on PIII
F(2) on PIII
5000 5050
5250
5350
5950
6050 Hz

FIGURE 6b

^{31}P SPECTRUM OF



P^{III} SPECTRUM

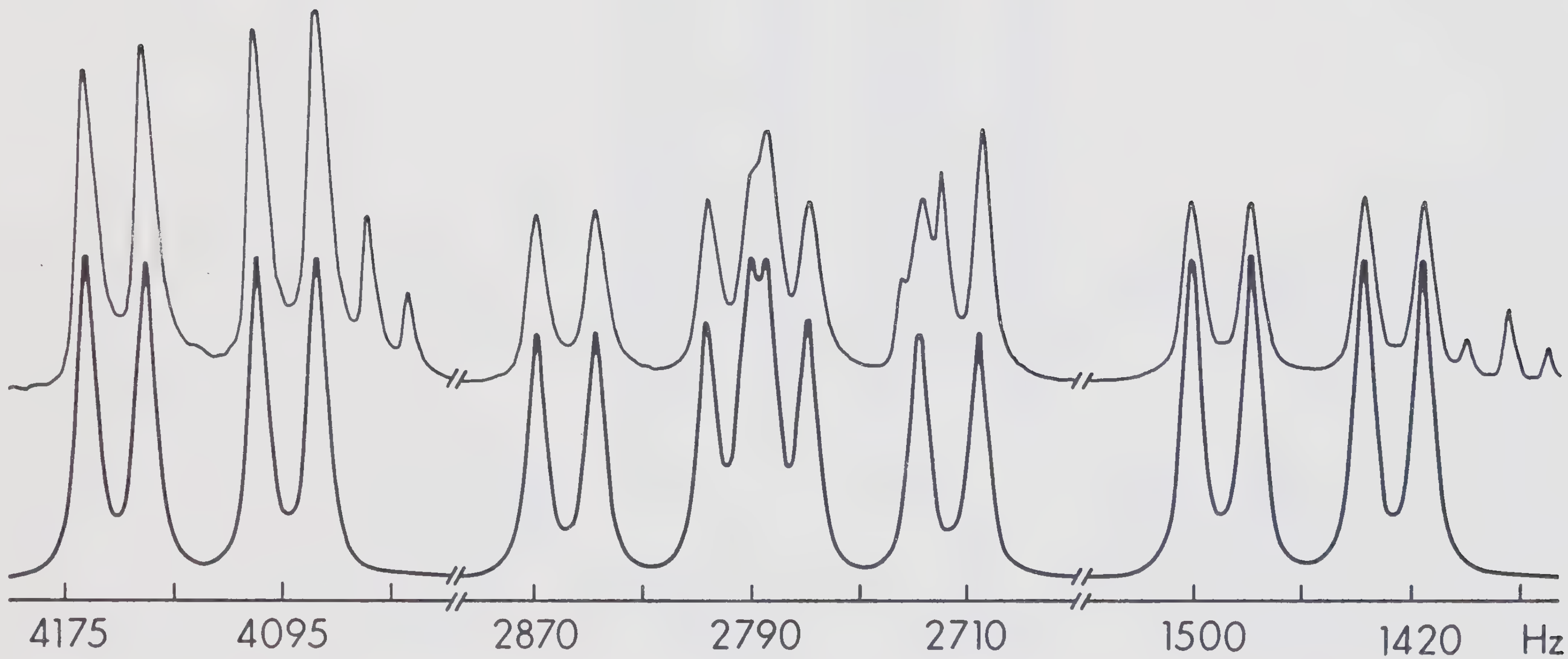


FIGURE 6c

HALF OF P^V SPECTRUM OF

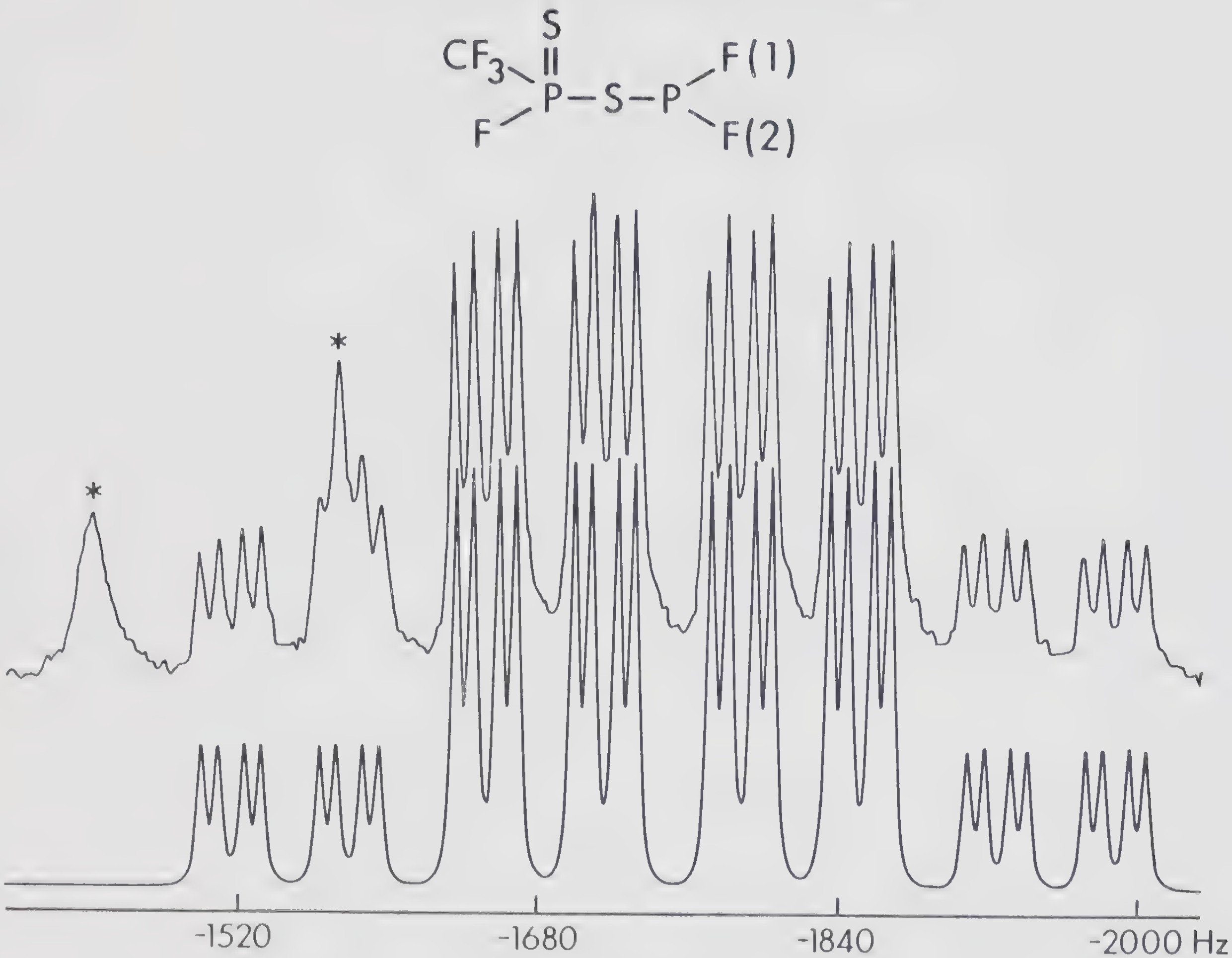
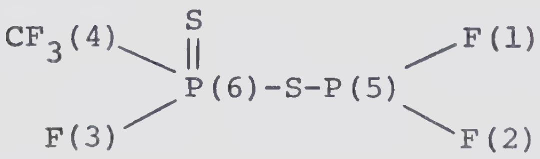


FIGURE 6d

TABLE 5

Nmr Coupling and Chemical Shift Parameters for

$CF_3(F)P(S)SPF_2$ (VI)



(VI)

coupling constants (Hz)

1-2 = 92.5				
1-3 = 6.0	2-3 = 7.0			
1-4 = 0.0	2-4 = 0.0	3-4 = 2.6		
1-5 = 1370.0	2-5 = 1291.0	3-5 = 22.0	4-5 = 0.0	
1-6 = 9.0	2-6 = 23.0	3-6 = 1174.0	4-6 = 136.0	5-6 = 63.0

chemical shifts [a]			linewidths (Hz)
ϕ_1 = 4645.0	Hz	(49.4 ppm)	L_1 = 5.0
ϕ_2 = 5344.0	Hz	(56.8 ppm)	L_2 = 5.0
ϕ_3 = 4453.0	Hz	(47.4 ppm)	L_3 = 4.0
ϕ_4 = 6980.0	Hz	(74.2 ppm)	L_4 = 2.4
ϕ_5 = 2785.0	Hz	(-76.5 ppm)	L_5 = 8.0
ϕ_6 = -1420.0	Hz	(39.0 ppm)	L_6 = 5.0

a) ^{19}F shifts from CF_2Cl_2 at 94.1 MHz.

^{31}P shifts from P_4O_6 at 36.4 MHz

due to coupling to P^V and to the fluorine atom on P^V (Figure 6a) but the lines arising from the three fluorine atoms bound directly to phosphorus are not so easily assigned (Figure 6b). Observation and measurement of two unique F-P^{III} coupling constants in the ^{31}P spectrum of trivalent phosphorus (Figure 6c) which gives rise to doublets of doublets in this region due to the two non-equivalent couplings to fluorine and to $^2J_{PP}$, and determination of the magnitude of the F-P^V coupling constant from the spectrum of P^V (Figure 6d), eventually enabled assignment of the fluorine spectra. It is seen in Table 5 that all three fluorine atoms have similar chemical shifts and Figure 6b shows that the lines arising from F on P^V are not well separated from those due to F on P^{III}. The spectra of the two fluorine atoms on P^{III} were calculated on the basis of an ABX system with first order couplings of different magnitudes for the two atoms to P^V and to F on P^V. In contrast to V where the non-equivalent CF_3 groups were considered to form an A_3B_3X spin system where $J_{AX} = J_{BX}$, in VI, $J_{AX} \neq J_{BX}$. The large chemical shift difference between the non-equivalent fluorine atoms as compared to the coupling between them ($\Delta/J = 7.6$) allows an almost first order interpretation of the ABX system for this compound. The fluorine atom on P^V interacts with every other magnetic nucleus in the molecule giving rise to large numbers of overlapping lines which cannot be re-

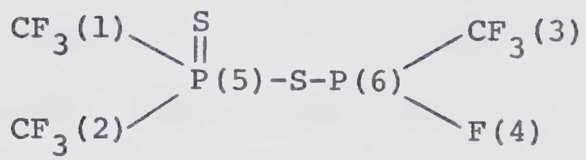
solved. Thus a rather broad doublet of doublets due to $^{1}J_{FP}$ and $^{3}J_{FP}$ results and no further coupling information can be extracted from these resonances. The previously mentioned spectrum of the trivalent phosphorus atom is seen to contain extra lines from ^{31}P transitions in $F_2P(S)SPF_2$ (I) which is present as impurity. The major features of the spectrum of P^V are a large doublet due to $^{1}J_{FP}$ which is further split into quartets of doublets by $^{2}J_{FP}$ and $^{2}J_{PP}$. Additional first order couplings of unequal magnitudes to the non-equivalent fluorine atoms on P^{III} give rise to the further doublet of doublets structure. It should be noted as in the previous case that although each of the non-equivalent groups in these molecules can be definitely assigned a complete and unique set of couplings to other nuclei in the molecule and a chemical shift value, no assignment of stereochemical orientation of the groups can be made or is implied.

3. <u>Bis(trifluoromethyl)thiophosphoryl-μ-thiofluoro(trifluoromethyl)phosphine (VII)</u>.

Spectral non-equivalence of the two CF_3 groups bound to P^V is made possible by a chiral trivalent phosphorus centre in $(CF_3)_2P(S)SP(F)CF_3$ since inversion of P^{III} is slow. The chemical shift difference (18.2 Hz) and spin-spin interaction (7.2 Hz) between the non-equivalent groups which are shown in Table 6 give rise to a value of

TABLE 6

Nmr Coupling and Chemical Shift Parameters for $(CF_3)_2P(S)SP(F)CF_3$ (VII)



(VII)

coupling constants (Hz)

1-2 = 7.2				
1-3 = 0.0	2-3 = 0.0			
1-4 = 1.4	2-4 = 0.0	3-4 = 3.4		
1-5 = 112.5	2-5 = 112.5	3-5 = 0.0	4-5 = 3.8	
1-6 = 6.0	2-6 = 2.5	3-6 = 77.8	4-6 = 1161.2	5-6 = 92.4

chemical shifts (Hz)[a]		linewidths
ϕ_1 = 5300.0	(62.6 ppm)	L_1 = 1.4
ϕ_2 = 5318.2	(62.8 ppm)	L_2 = 1.4
ϕ_3 = 4751	(56.1 ppm)	L_3 = 1.0
ϕ_4 = 13432	(158.8 ppm)	L_4 = 2.0
ϕ_5 = -2448	(67.3 ppm)	L_5 = 0.8
ϕ_6 = +1259	(-34.6 ppm)	L_6 = 1.0

---

a) ^{19}F shifts from CF_2Cl_2 at 84.6 MHz

^{31}P shifts from P_4O_6 at 36.4 Hz.

Δ/J of 2.5. This clearly results in a second order spectrum of the A_3B_3X type which is shown in Figure 7a. As in V, J_{AX} and J_{BX} are the same and can be measured from the ^{31}P spectra leaving only J_{AB} and the chemical shifts ϕ_A and ϕ_B to be determined directly from this region of the spectrum in order to duplicate its major features. Couplings to other parts of the molecule are extremely difficult to extract from this region but often show up very clearly in the spectra of these other parts. Thus the nmr spectrum of the pentavalent phosphorus atom (Figure 7b) consists of a doublet of septets due to coupling to P^{III} and to the two CF_3 groups, and is split further by a small interaction with the single fluorine atom on P^{III} to yield $^2J_{FP}$ (J_{AX}, J_{BX}) of 112.5 Hz. Similarly the trivalent phosphorus spectrum (Figure 7c) is split into a doublet by the large coupling to the single fluorine atom bound to it and further split into doublets of quartets by P^V and the CF_3 group on P^{III}. The extra fine structure in the nmr spectrum can only be explained by unequal couplings to the non-equivalent CF_3 groups on P^V. The various interactions of the non-equivalent groups determined from the ^{31}P spectra and guesses as to the chemical shifts of these groups and the coupling between them still left their spectra with unexplained minor features which could only arise from coupling to the substituents on P^{III}. Since the nmr spectrum of CF_3 on P^{III} (Figure 7d) consisted only

FIGURE 7. Observed and calculated ^{19}F and ^{31}P spectrum of $(CF_3)_2P(S)SP(F)CF_3$ (VII) obtained in 30% v/v CF_2Cl_2 solution. ^{19}F spectrum obtained at 20°C at 84.6 MHz with CF_2Cl_2 as both lock and reference compound. ^{31}P spectra obtained at 20°C at 36.4 MHz with CF_2Cl_2 as reference compound and P_4O_6 as external reference. Impurity lines marked by asterisks.

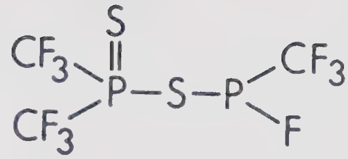
7a ^{19}F spectral region due to CF_3 on P^V. Impurity lines not identified.

7b ^{31}P spectrum of P^V region.

7c Half of ^{31}P spectrum of P^{III} region.

7d ^{19}F spectral region due to CF_3 on P^{III}.

7e ^{19}F spectral region due to F on P^{III}

^{19}F SPECTRUM OF 

CF_3 on P^V

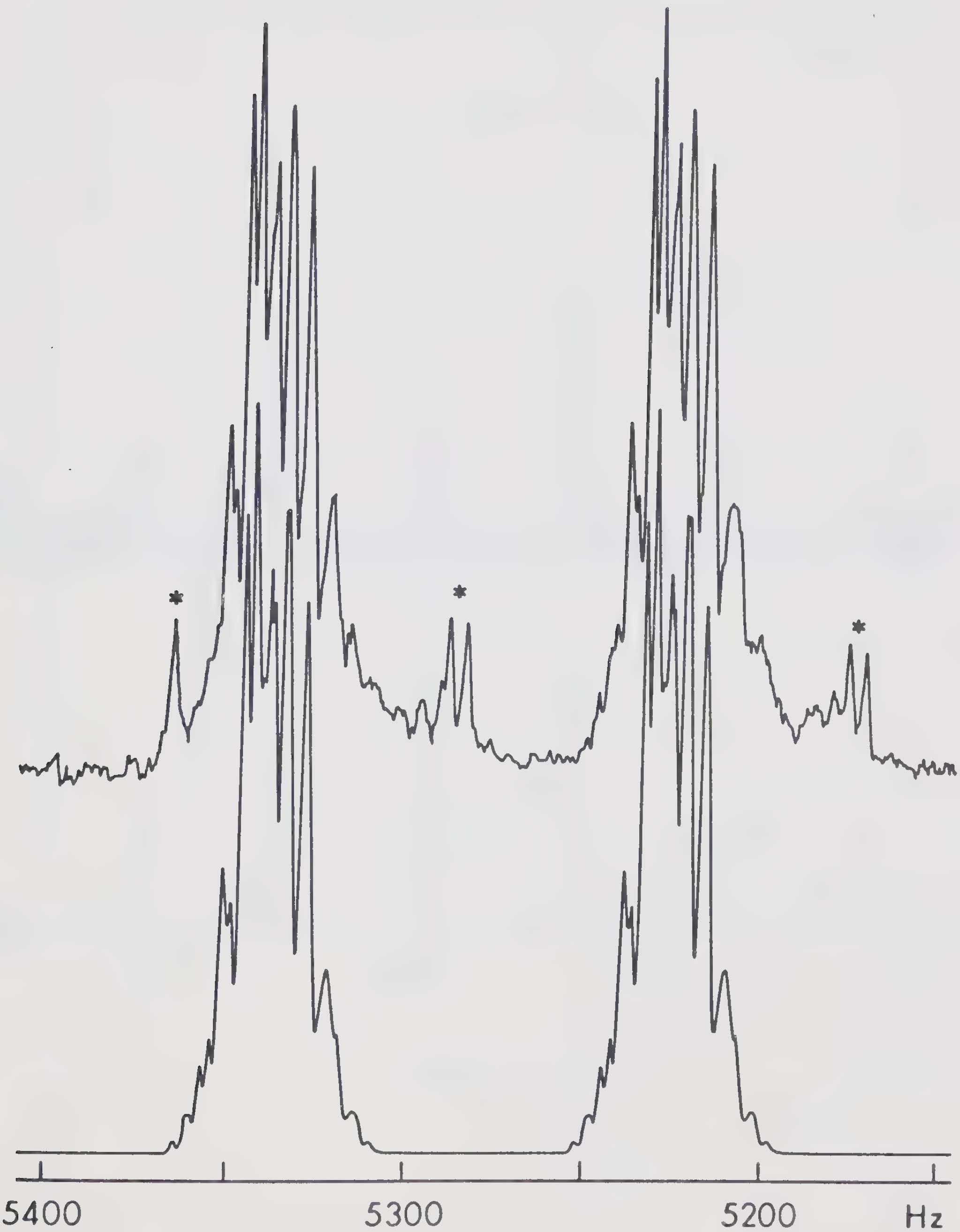
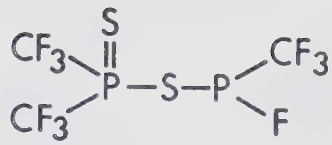


FIGURE 7a

^{31}P SPECTRUM OF 

P^V SPECTRUM

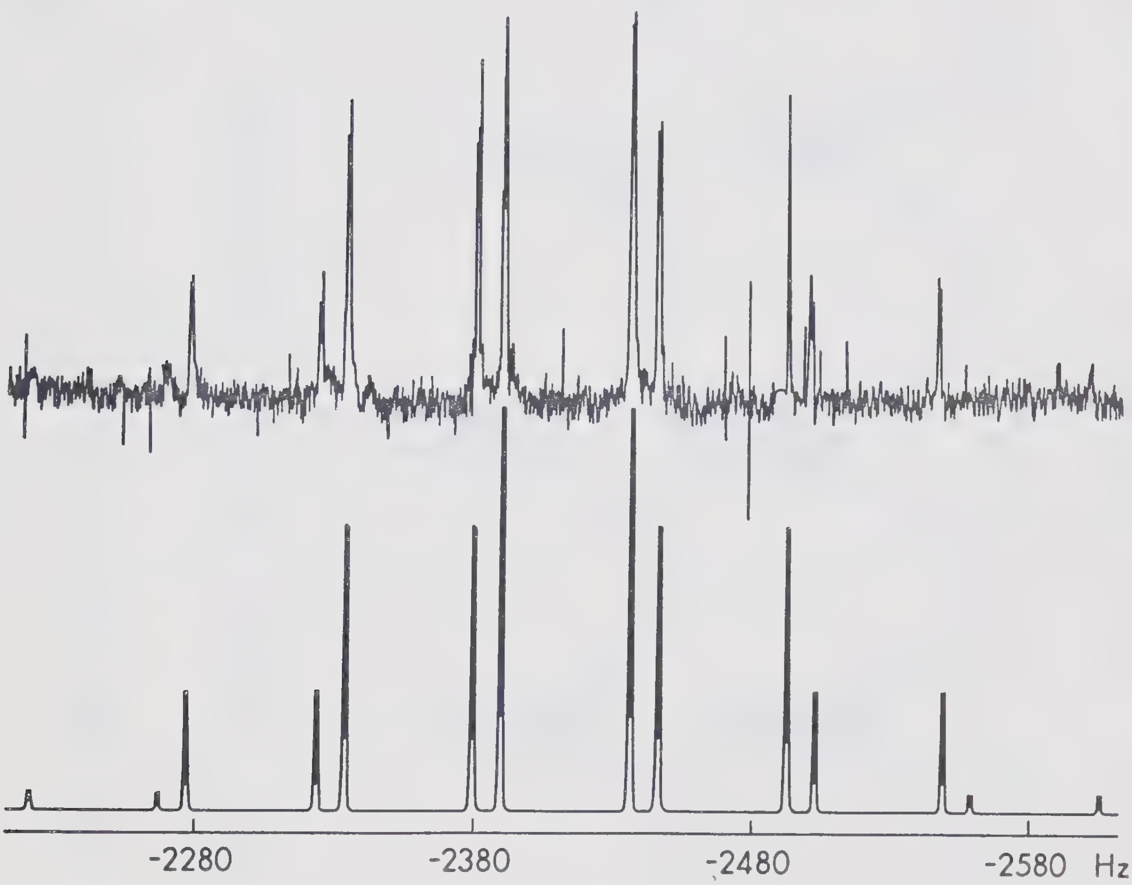
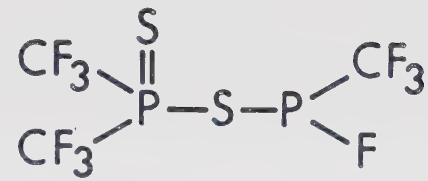


FIGURE 7b

^{31}P SPECTRUM OF 

HALF OF P^{III} SPECTRUM

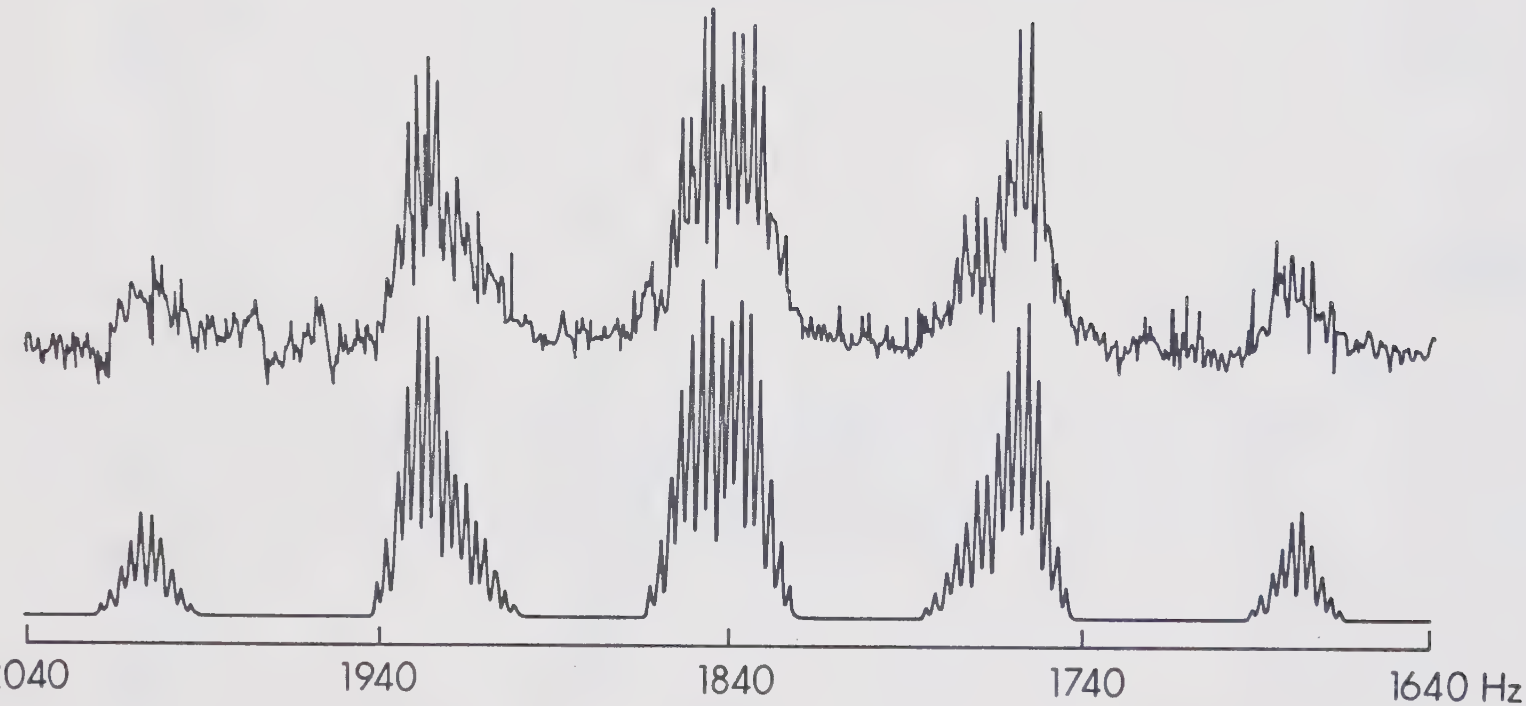
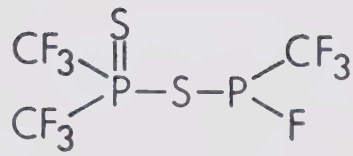


FIGURE 7c

^{19}F SPECTRUM OF 

CF_3 on P^{III}

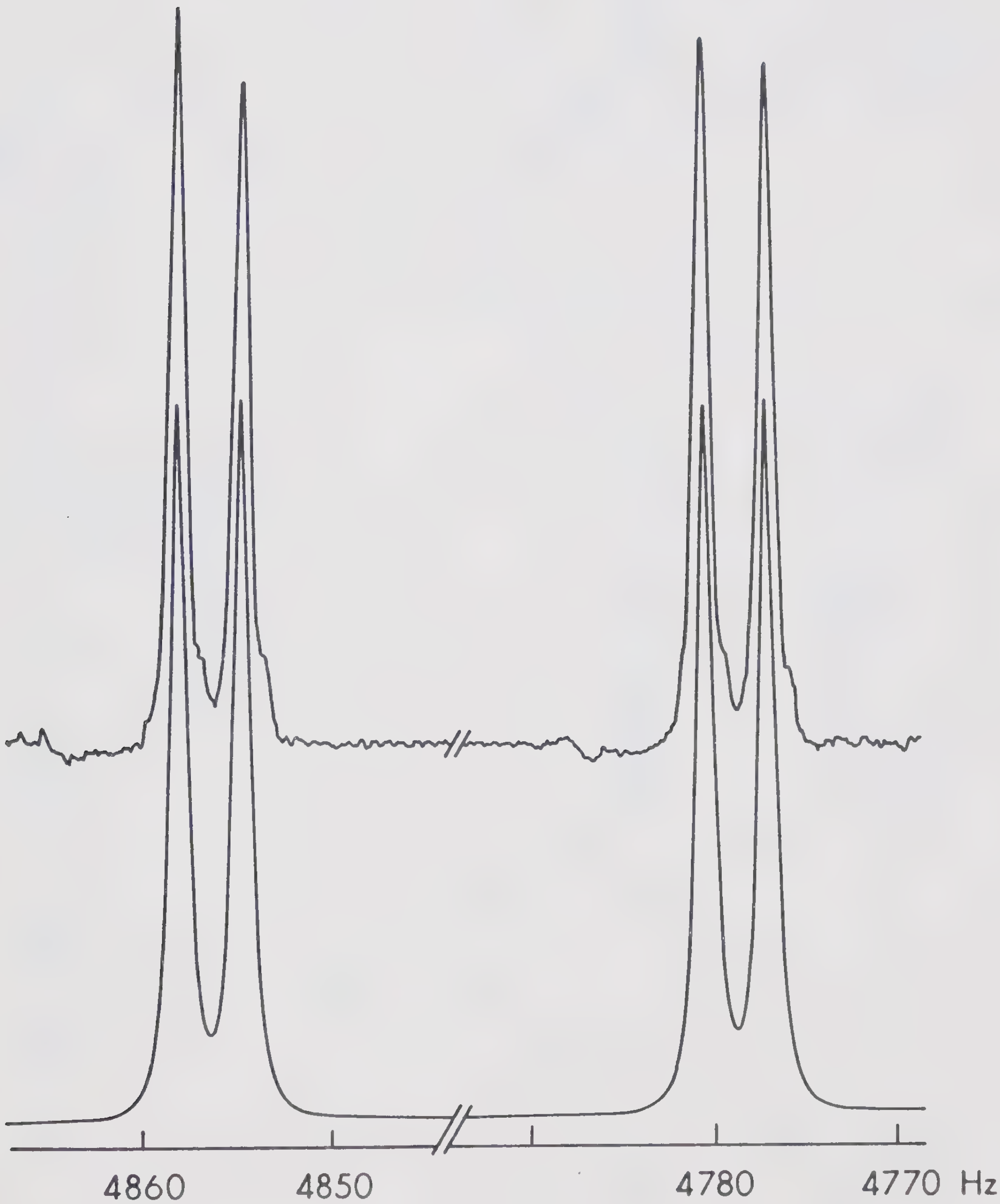
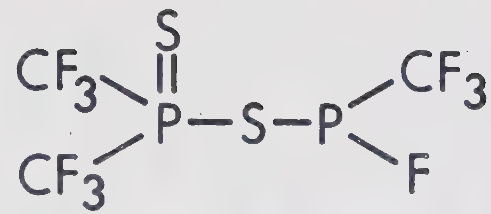


FIGURE 7d

^{19}F SPECTRUM OF 

F on P^{III}

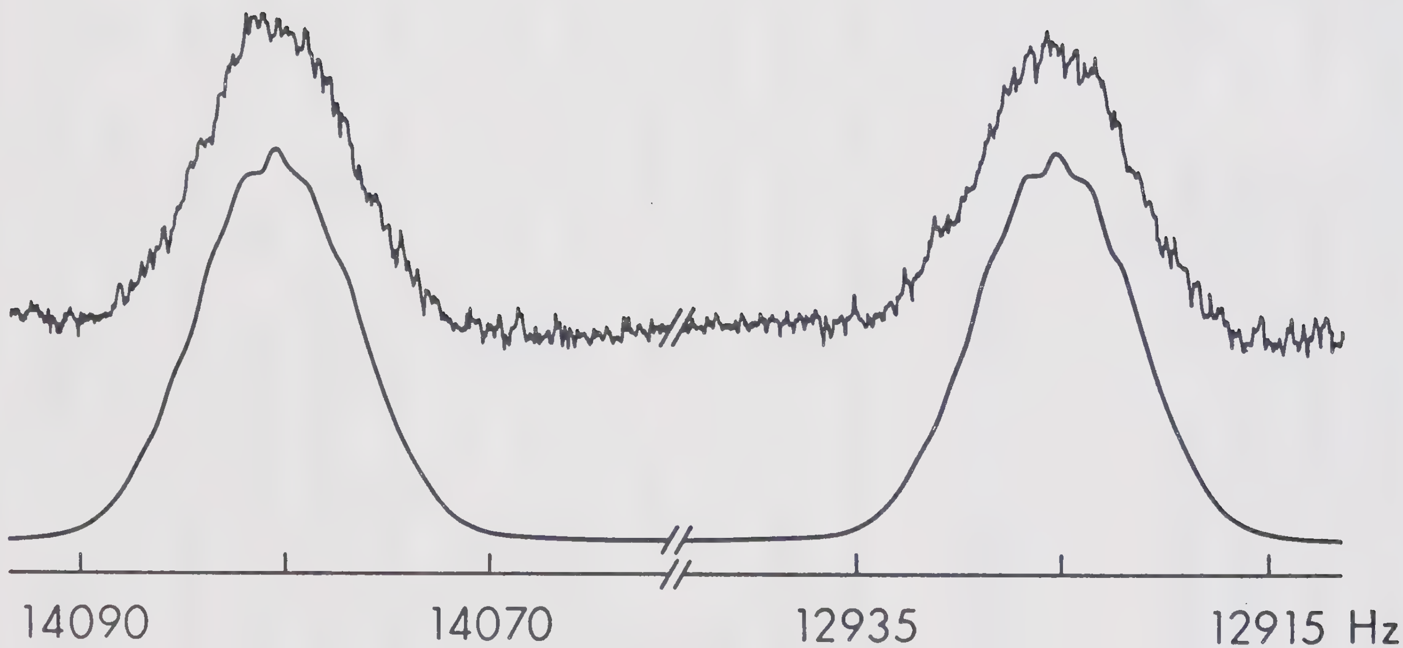


FIGURE 7e

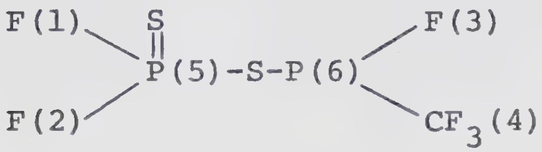
of a doublet of doublets due to coupling to P^{III} and to the single fluorine atom, this fine structure must result from interaction with the fluorine atom whose spectrum is not resolved because of the large number of overlapping transitions (Figure 7e). Thus these couplings have been determined by achieving a best fit of calculated results to observed spectra of CF_3 joined to P^V.

4. <u>Difluorothiophosphoryl-μ-thiofluoro(trifluoromethyl)-phosphine (VIII)</u>

The last of the mixed valence compounds prepared in this study which possess non-equivalent groups due to a chiral phosphorus centre is $F_2P(S)SP(F)CF_3$ whose nmr spectrum is shown in Figure 8. Table 7 lists the nmr parameters extracted from these spectra. The fluorine atoms on P^V form the AB part of an ABX spin system with $\Delta/J = 2.2$ (Figure 8a and 8b). As in its isomer (VI) two different one-bond F-P coupling constants are observed for the non-equivalent fluorine nuclei but in this case the difference in their magnitudes is much less. The major features of the region of the spectrum due to F on P^V consist of two pseudo-quartets. The quartet structure is due to the AB spin system where two lines may be assigned to nucleus A and two lines to nucleus B. The large interactions of the A and B nuclei (the two non-equivalent fluorine atoms) with the X nucleus (P^V) then splits each pair of two lines by the

TABLE 7

Nmr Coupling and Chemical Shift Parameters for $F_2P(S)SP(F)CF_3$ (VIII)



(VIII)

coupling constants (Hz)

1-2 = 82.5				
1-3 = 8.8	2-3 = 1.3			
1-4 = 0.0	2-4 = 1.3	3-4 = 4.2		
1-5 = 1224.0	2-5 = 1203.0	3-5 = 1.2	4-5 = 0.0	
1-6 = 0.5	2-6 = 16.3	3-6 = 1154.0	4-6 = 72.6	5-6 = 104.7

chemical shifts (Hz)[a]	linewidths (Hz)
ϕ_1 = 957 (10.2 ppm)	L_1 = 1.0
ϕ_2 = 1140 (12.1 ppm)	L_2 = 1.0
ϕ_3 = 15173 (161.2 ppm)	L_3 = 1.0
ϕ_4 = 5472 (58.2 ppm)	L_4 = 3.6
ϕ_5 = -1138 (31.3 ppm)	L_5 = 2.0
ϕ_6 = 1357 (-37.2 ppm)	L_6 = 2.6

a) ^{19}F shifts from CF_2Cl_2 at 94.1 MHz

^{31}P shifts from P_4O_6 at 36.4 MHz

FIGURE 8. Observed and calculated ^{19}F and ^{31}P spectrum of $F_2P(S)SP(F)CF_3$ (VIII) obtained in 30% v/v CF_2Cl_2 solution at -80°C. ^{19}F spectrum obtained at 94.1 MHz with CF_2Cl_2 as both lock and reference compound. ^{31}P spectrum obtained at 36.4 MHz with CF_2Cl_2 as lock compound and P_4O_6 as external reference.

8a Low field half of ^{19}F spectral region arising from F on P^V.

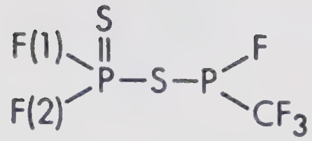
8b High field half of ^{19}F spectral region arising from F on P^V.

8c ^{19}F spectral region due to CF_3 on P^{III}.

8d Low field half of ^{19}F spectral region arising from F on P^{III}

8e Central portion of ^{31}P spectral region due to P^V.

8f Half of ^{31}P spectral region due to P^{III}.

^{19}F SPECTRUM OF 

F ON P^V (LOW FIELD)

EXPANSION OF F(2) LOW FIELD SPECTRUM

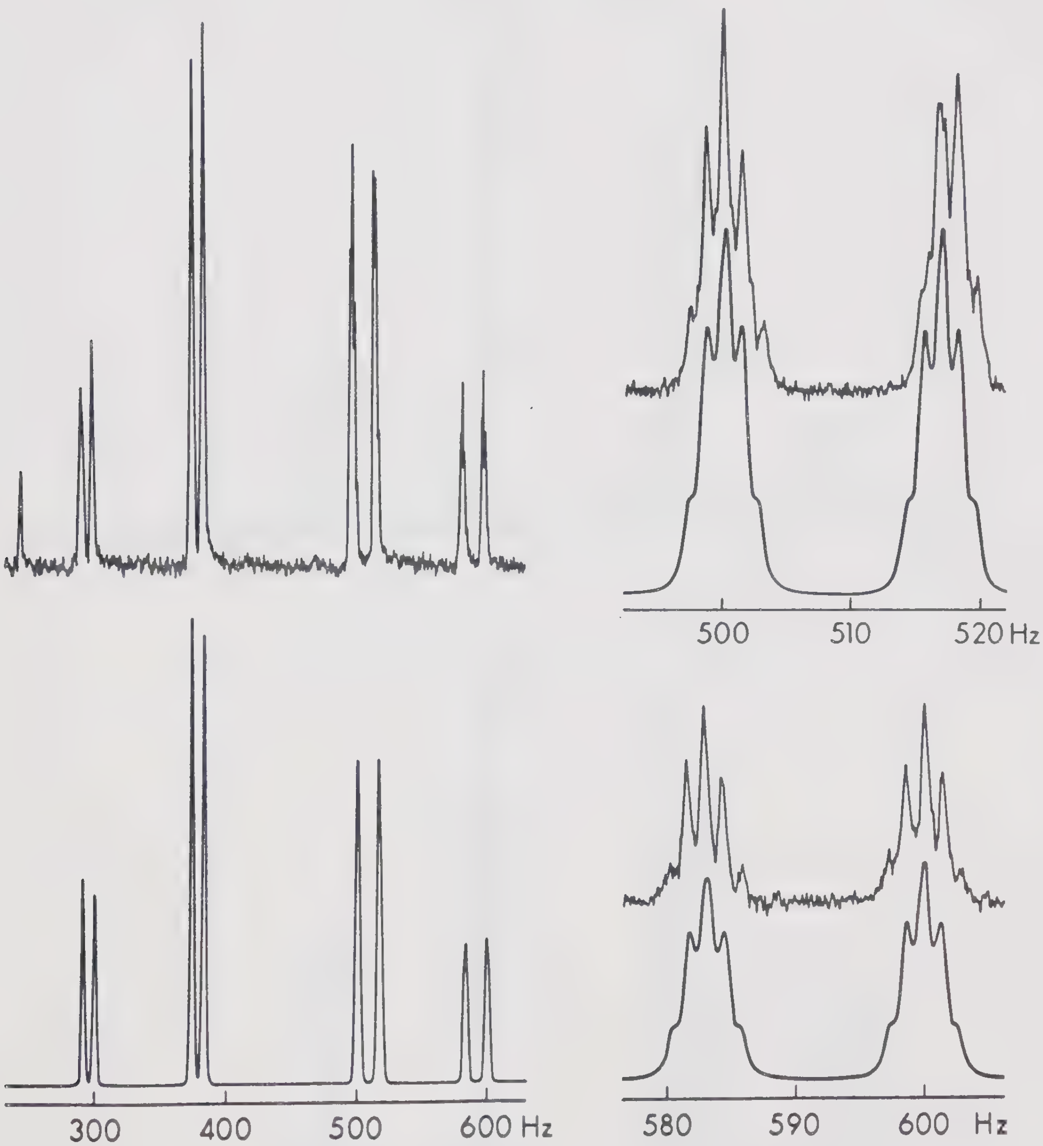
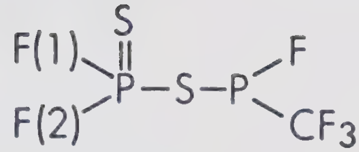


FIGURE 8a

^{19}F SPECTRUM OF 

F ON P^V (HIGH FIELD)

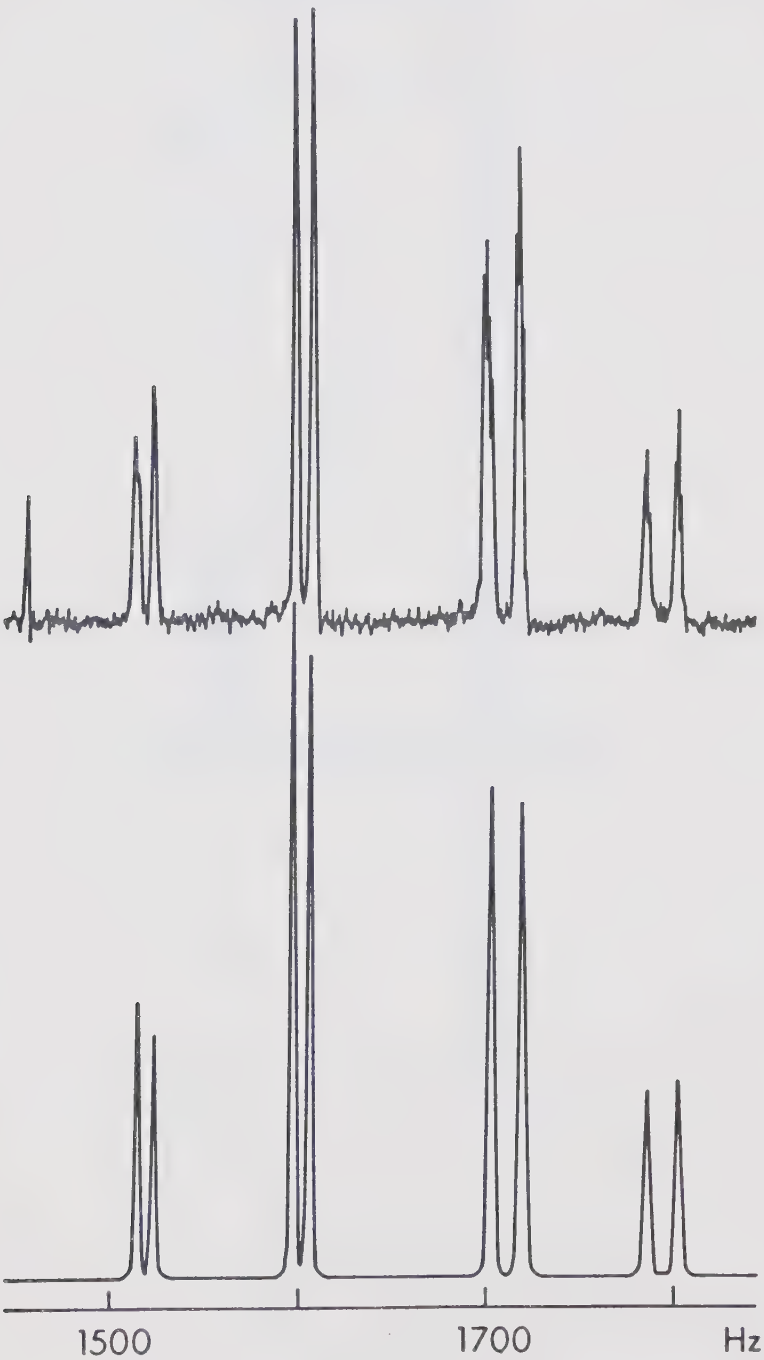
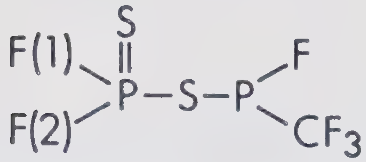


FIGURE 8b

^{19}F SPECTRUM OF



CF_3 REGION

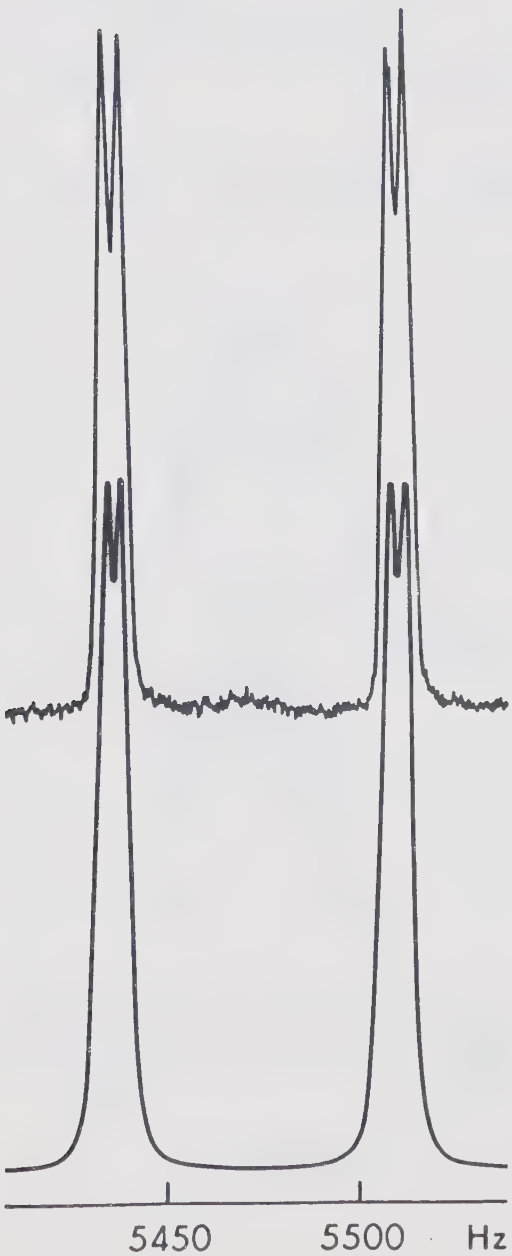
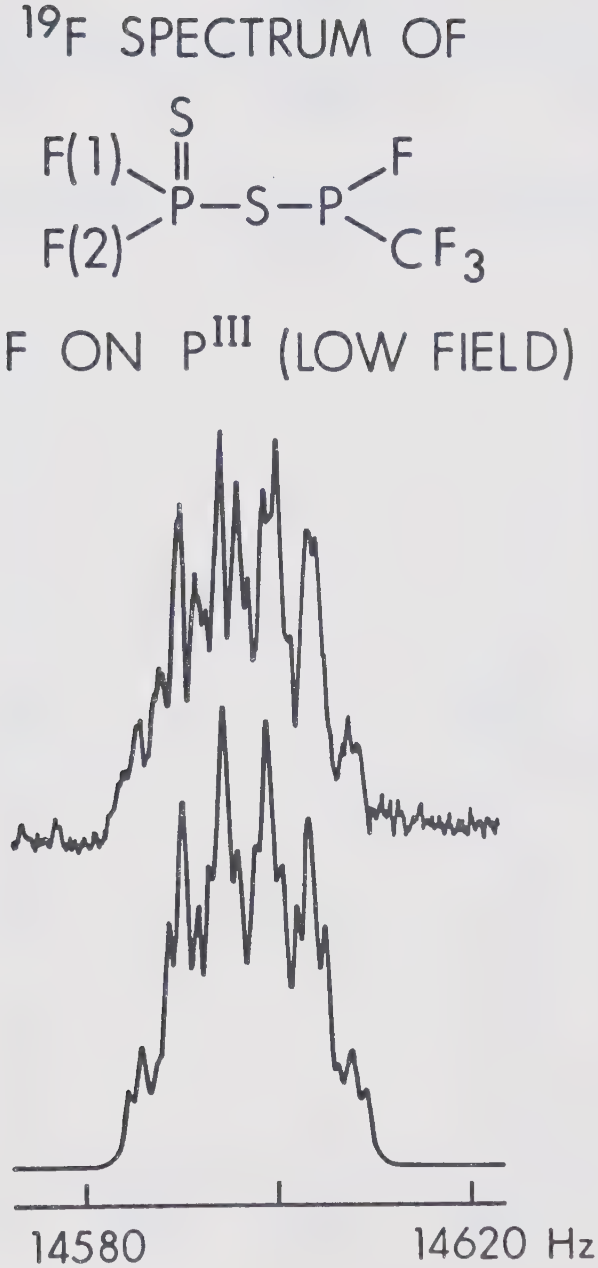
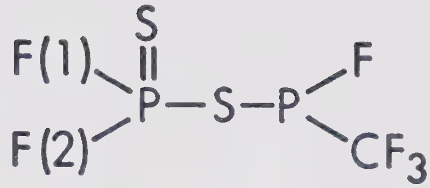


FIGURE 8c



^{19}F SPECTRUM OF
S
F(1)
F(2)
P—S—P
F
CF_3
F ON P^{III} (LOW FIELD)
14580
14620 Hz

FIGURE 8d

^{31}P SPECTRUM OF 

P^V SPECTRUM (CENTRAL PORTION)

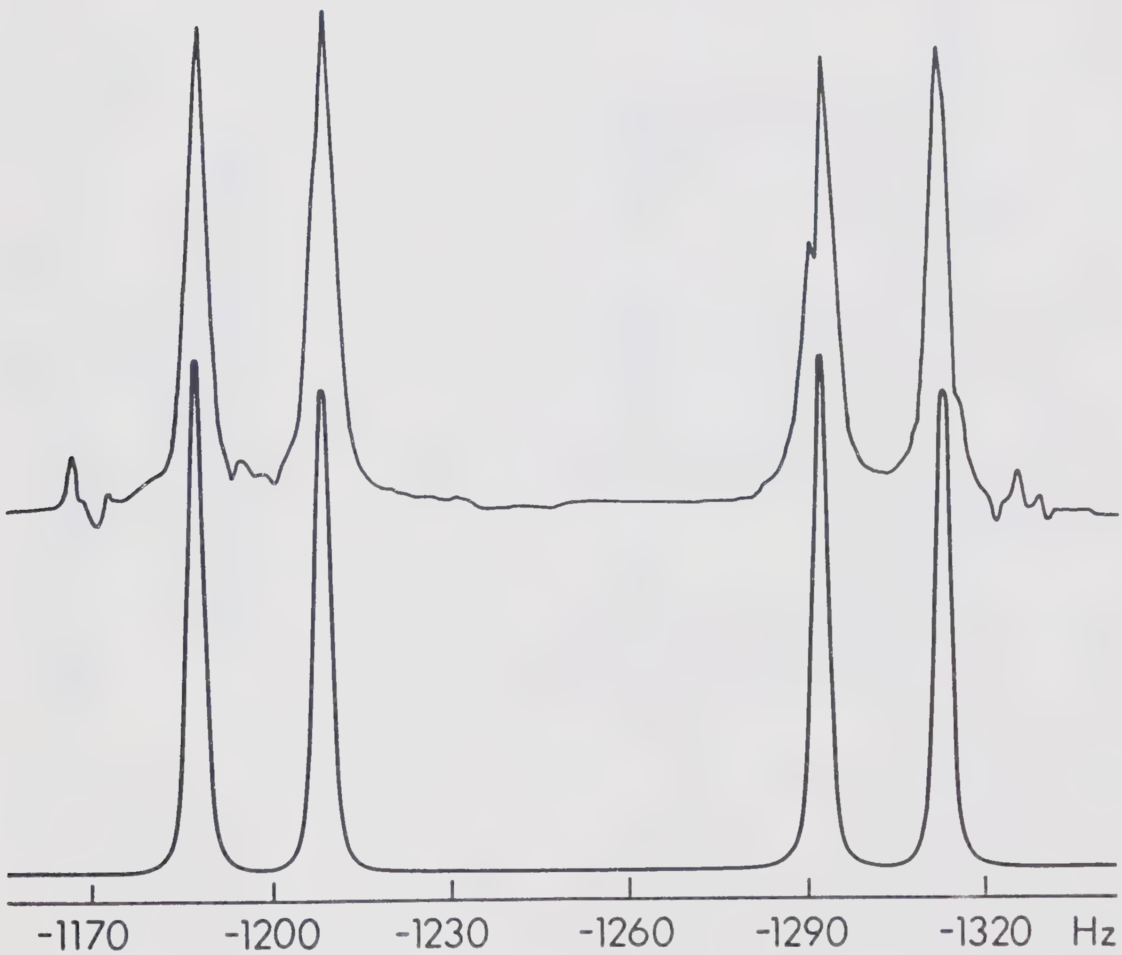
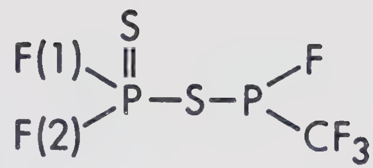


FIGURE 8e

^{31}P SPECTRUM OF 

HALF OF P^{III} SPECTRUM

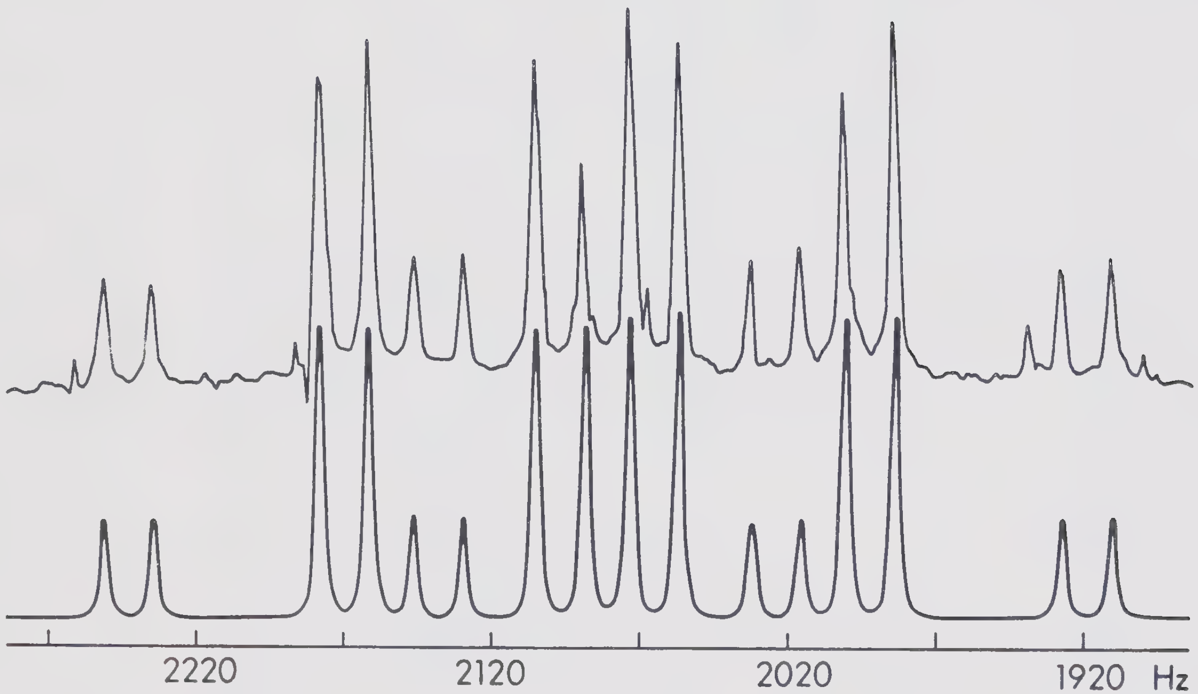


FIGURE 8f

appropriate value of $^{1}J_{FP}$ and yields the two quartets whose spacings are not the same. Further couplings are then superimposed on these lines in a first-order manner. It is seen in Figures 8a and 8b that each of the lines in both quartets is further split into a doublet. This splitting results for one nucleus from interaction with P^{III} and for the other from coupling to F on P^{III}. Thus two lines in each quartet which arise from the A nucleus are split by 8.8 Hz due to coupling to fluorine and the other two lines are split by 16.3 Hz from coupling of the B nucleus to P^{III}. Further first order couplings to the fluorine atom and trifluoromethyl group are also observed although in the case of coupling to CF_3, this is not observed in the spectrum of CF_3 since it is obscured by the rather large linewidth of transitions from this grouping. Thus the spectrum of the CF_3 grouping (Figure 8c) appears as a doublet of doublets due to interaction with P^{III} and with F on P^{III}. The spectrum of the fluorine atom on P^{III} (Figure 8d) is fairly well resolved and shows the expected couplings.

The pentavalent phosphorus atom is coupled to each of the fluorine atoms bound to it by different magnitudes resulting in a doublet of doublets in its spectrum (Figure 8e). Further coupling to P^{III} splits each of these lines into doublets but the small interaction with F on P^{III} which is observed in the fluorine spectrum is not seen due

to the magnitude of the P^V linewidths.

The spectrum of P^{III} (Figure 8f) consists of a large doublet from coupling to the directly bound fluorine atom. Further first order couplings to CF_3 and P^V yield a doublet of quartets and interaction with one of the fluorine atoms on P^V splits each of these lines into a doublet.

5. Fluoro(trifluoromethyl)thiophosphoryl-μ-thiodifluror-(trifluoromethyl)phosphine (IX, X).

The final member of this series of mixed valence compounds, $CF_3(F)P(S)SP(F)CF_3$, was prepared from $CF_3(F)PS_2H$ and $CF_3(F)PN(CH_3)_2$ and was found to be a mixture of two racemates which give rise to different nmr spectra. Since both starting materials consisted of mixtures of d and l optical isomers, four mixed valence compounds of the same stoichiometry but different stereochemistry resulted. The four isomers may be labelled dd', dl', ld' and ll' and of these dd' and ll' form one racemate and dl' and ld' are the other. The racemic mixtures are distinguishable from one another in the nmr but the components of a particular mixture are not. The Newman projections given in Figure 9 show one component of each of the racemates and it can be seen that any atom in one of the configurations is always in a different magnetic environment than the corresponding nucleus in the other configuration.

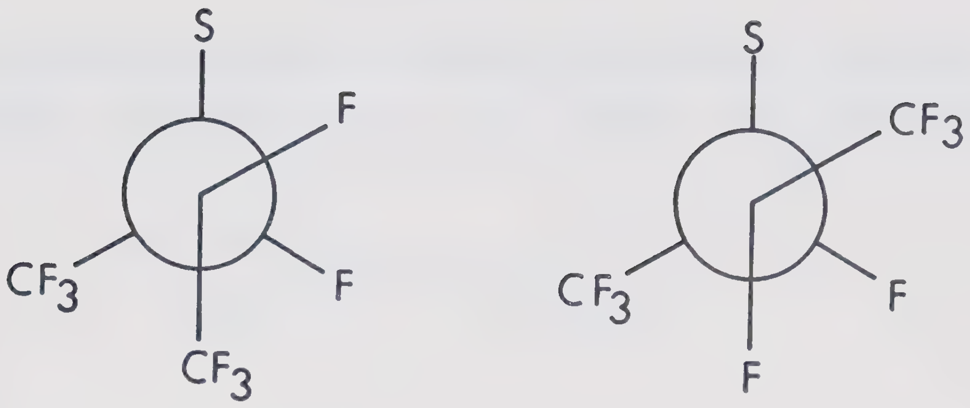


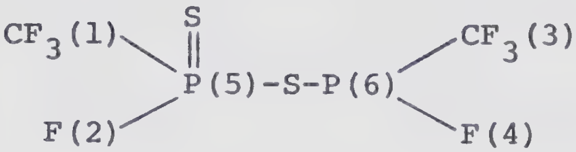
FIGURE 9 Newman Projections of the Isomers of $CF_3(F)P(S)SP(F)CF_3$ (IX and X)

Parts of the nmr spectra of the two racemates are shown in Figure 10 and the nmr parameters which could be measured are given in Tables 8 and 9. Structures shown throughout the thesis for these molecules such as in Tables 8 and 9, do not imply their absolute stereochemistry but only that the two racemates are different.

The recently prepared compounds $CF_3(CH_3)PP(CH_3)CF_3$ [56] and $CF_3(CH_3)PSP(CH_3)CF_3$ [58] are other examples of phosphorus compounds which show optical isomerism. These compounds, whose nmr spectra have been partially analysed, were found to exist as a dl racemic mixture and in a meso form due to their symmetry. The series of compounds R(F)P(S)SP(S)(F)R, where R is CH_3-, CH_3CH_2-, or C_6H_5- [69], also exhibit optical isomerism and in the methyl substituted compound the nmr spectrum has been completely solved. In the ethyl and

TABLE 8

Nmr Coupling and Chemical Shift Parameters of the Major Component of the Mixture of the Isomers of $CF_3(F)P(S)SP(F)CF_3$



(IX)

coupling constants (Hz)

1-2 = 2.8				
1-3 = 0	2-3 = 0			
1-4 = 1.2	2-4 = n.r.	3-4 = 5.0		
1-5 = 134	2-5 = 1165	3-5 = 0	4-5 = 5	
1-6 = 5.2	2-6 = n.r.	3-6 = 74	4-6 = 1156	5-6 = 86

chemical shifts (Hz)[a]

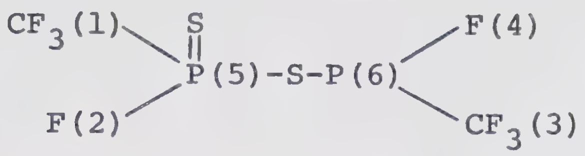
ϕ_1 =	6415	(68.2 ppm)
ϕ_2 =	5007	(53.2 ppm)
ϕ_3 =	5431	(57.7 ppm)
ϕ_4 =	14955	(158.9 ppm)
ϕ_5 =	-1041	(28.6 ppm)
ϕ_6 =	1370	(-38 ppm)

a) ^{19}F shifts from CF_2Cl_2 at 94.1 MHz

^{31}P shifts from P_4O_6 at 36.4 MHz

TABLE 9

Nmr Coupling and Chemical Shift Parameters of the Minor Component of the Mixture of the Isomers of $CF_3(F)P(S)SP(F)CF_3$



(X)

coupling constants (Hz)

1-2 = 2.8				
1-3 = 0	2-3 = 0			
1-4 = <0.5	2-4 = n.r.	3-4 = 4.3		
1-5 = 134	2-5 = 1180	3-5 = 0	4-5 = 4	
1-6 = 2.8	2-6 = n.r.	3-6 = 75	4-6 = 1148	5-6 = 103

chemical shifts (Hz)[a]

ϕ_1 = 6453	(68.6 ppm)
ϕ_2 = 4985	(53.0 ppm)
ϕ_3 = 5428	(57.7 ppm)
ϕ_4 = 15101	(160.5 ppm)
ϕ_5 = -1115	(30.6 ppm)
ϕ_6 = 1370	(-38 ppm)

a) ^{19}F shifts from CF_2Cl_2 at 94.1 MHz

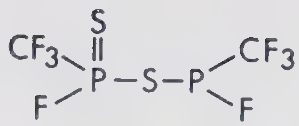
^{31}P shifts from P_4O_6 at 36.4 MHz

FIGURE 10. Observed and Calculated partial ^{19}F and ^{31}P spectra of the isomers of $CF_3(F)P(S)SP(F)CF_3$ (IX and X) obtained in 20% v/v CF_2Cl_2 solution. ^{19}F spectrum obtained at 94.1 MHz with CF_2Cl_2 as both lock and reference compound. ^{31}P spectrum determined at 36.4 MHz at -50°C with CF_2Cl_2 as lock compound and P_4O_6 as the external reference.

10a -50°C and -100°C ^{19}F spectra of the region due to CF_3 on P^{III}.

10b -50°C ^{19}F spectral region due to CF_3 on P^V.

10c Half of ^{31}P spectral region due to P^V

^{19}F SPECTRUM OF 

CF_3 ON P^{III}

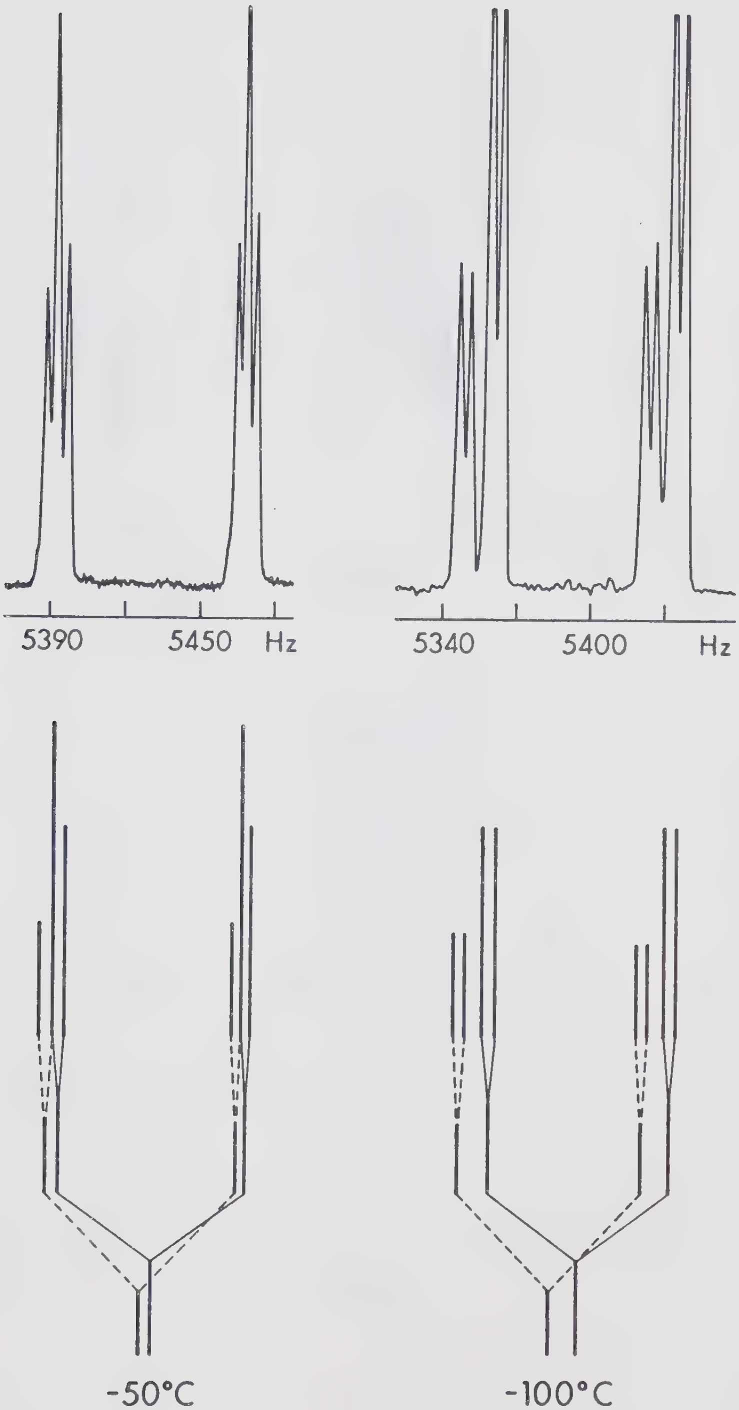
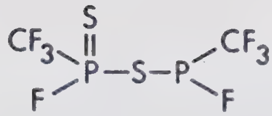


FIGURE 10a

^{19}F SPECTRUM OF 

CF_3 ON P^V

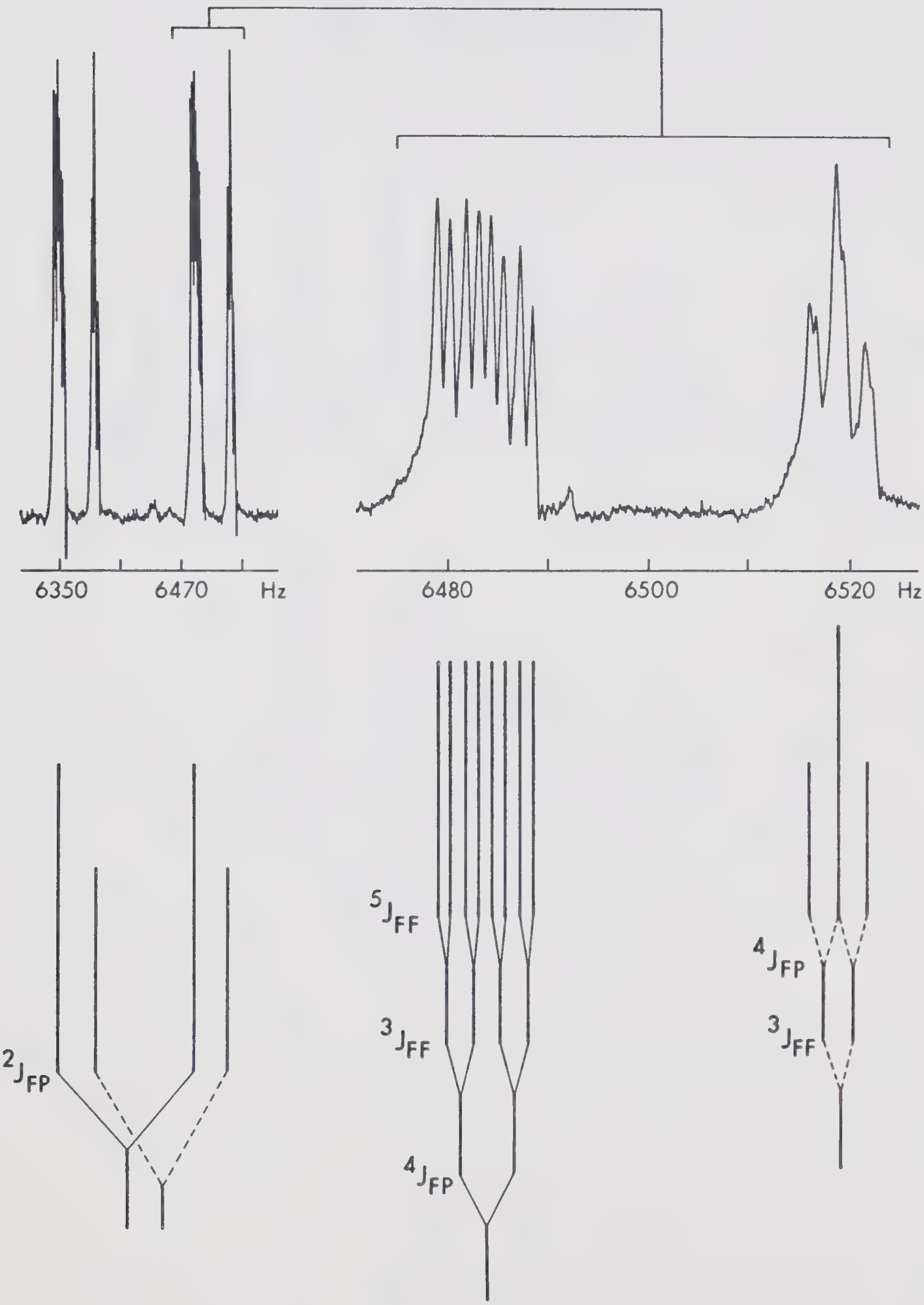
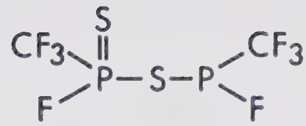


FIGURE 10b

^{31}P SPECTRUM OF 

HALF OF P^V REGION

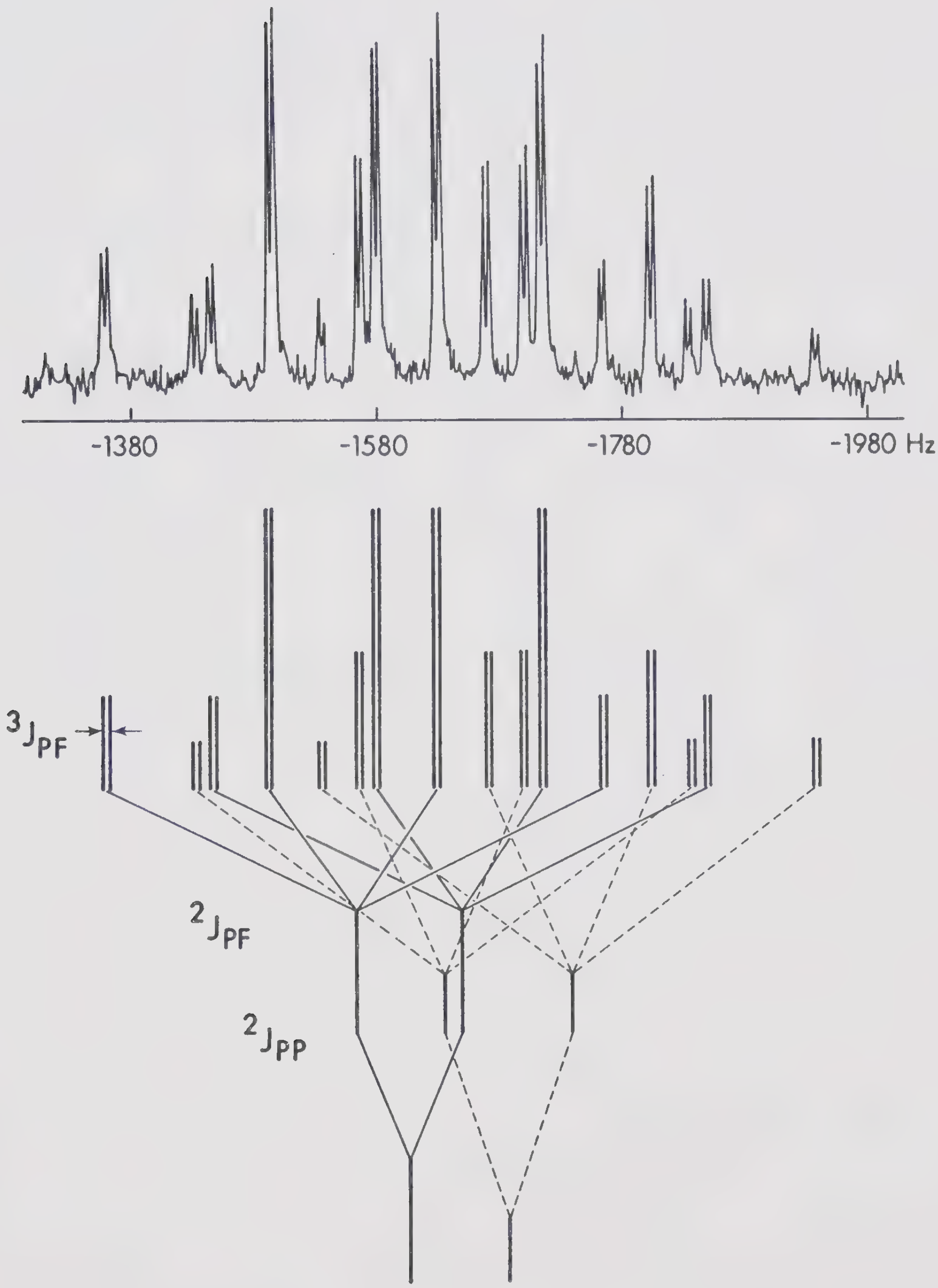


FIGURE 10c

phenyl derivatives, the proton nmr spectra were not fully analysed.

Solution of the nmr spectra of the mixture of racemates reported in this study (IX and X) unfortunately could not be carried to completion due to the poor resolution observed in the spectra of the single fluorine atoms bound to both P^{III} and P^{V}. The spectra of these nuclei are not shown in Figure 10 since only chemical shift information could be extracted from them. The extremely complicated first order spectra of the trivalent phosphorus nuclei could not be analysed due to the near-identical nature of the two racemates. This gives rise to nmr spectra that have nearly equal chemical shift values and large numbers of transitions arising from spin-spin coupling, many of which are thought to overlap with other transitions. A simple case of overlap is seen in the spectra of the CF_3 groups bound to P^{III} (Figure 10a) which appear as a doublet of triplets at -50°C. However, cooling the sample to -100°C results in the observation of two sets of doublets of doublets one of which arises from each of the racemates. The couplings, although unsubstantiated by their measurement from the spectra of the other nuclei, presumably arise from interaction with P^{III} and F on P^{III} respectively. In this region of the spectrum it is seen that one of the two racemic mixtures is in higher concentration than the other and it is this feature alone which allows assignment

of transitions in various regions of the spectrum to one particular racemate. Thus parameters for the high concentration component (IX) are given in Table 8 while those for the low concentration racemate (X) are listed in Table 9. Even at -50°C, the spectra of the CF_3 groups on P^V are well separated for the two mixtures (Figure 10b). In the major component (IX) this group is coupled to P^V resulting in a large doublet. These major peaks are further split into doublets of doublets of doublets by F on P^V, P^{III}, and F on P^{III}. Only tentative assignments of these interactions, based on similar couplings in the related molecules discussed previously, have been made because of the problems of resolution and assignment in the spectra of the single fluorine atoms and the trivalent phosphorus nucleus mentioned earlier. The spectrum of X shows a similar coupling of the trifluoromethyl group to P^V. Additional nearly equal couplings, apparently to F on P^V and to the trivalent phosphorus nucleus, give rise to a triplet structure. A very small coupling to F on P^{III} may also be present but is not resolved.

The nmr spectrum of the pentavalent phosphorus atoms (Figure 10c) yields nearly equal chemical shift values for IX and X but because the splittings these nuclei suffer are less extensive than those suffered by P^{III} and because they are of different magnitudes, their spectra are easily analysed. After coupling to the

directly bound fluorine which results in a widely spaced doublet, the P^{V} nuclei interact with the trifluoromethyl groups to which they are bound, with P^{III}, and with the fluorine atom on P^{III}. This results in a spectral pattern consisting of a doublet of quartets of doublets for each of the racemates.

DISCUSSION

1. Geminal non-equivalence in mixed valence compounds with chiral phosphorus centres.

The chemically non-equivalent species opposite the chiral phosphorus atom in all cases show unequal couplings to nuclei in other parts of the molecule. This is primarily due to the chirality of the phosphorus atom which puts each of the groups in a different magnetic environment. Another contributing factor may be restricted rotation about the bonds to the bridging sulfur atom. The latter effect could then lead to *cis* and *trans* interactions across the molecule which could explain the asymmetry of the fine structure in the spectra of $F_2P(S)SP(CF_3)_2$ (III) which is described in Chapter III of this thesis. The spectra of the previously reported compound (I) [21] show intensities which would not be expected if the two fluorine atoms on each of the phosphorus atoms are equivalent and the existence of *cis* and *trans* couplings may explain these variations. Better spectral resolution, not available at the low temperature limit of present spectrometers, appears necessary to comment further on this mechanism.

Perhaps the most interesting information obtained from the solution of the spectra of V, VI, VII, and VIII is the magnitude of the coupling between geminal fluorine atoms or geminal trifluoromethyl groups. Although these couplings

exist in all compounds with two or more of these groups bound to phosphorus, they may only be observed if the groups are made chemically or magnetically non-equivalent and the degree of non-equivalence should have very little effect on the magnitudes of such interactions. The chemical shift difference between two such groups however is a reflection of their non-equivalence. Thus the geminal CF_3-CF_3 coupling constant in V and VII is relatively constant at about 8 Hz whereas the chemical shift difference between the groups is a factor of two larger when they are joined to P^{III} than to P^{V}. The same behaviour is observed in VI and VIII where the geminal F-F coupling remains relatively constant at about 85 Hz. The chemical shift difference between the non-equivalent fluorine atoms is only 2 ppm in VIII which has a chiral P^{III} centre but increases markedly to over 7 ppm in VI where the chiral centre is a pentavalent phosphorus atom. In these two compounds, the non-equivalent atoms couple with different magnitudes to the phosphorus they are bound to and this difference is much greater in VI than in VIII. This difference in short range P-F coupling for the non-equivalent groups (in this case $^2J_{FP}$) is not observed in V and VII but this is probably due to the small magnitude of the effect due to the carbon atom intervening between F and P, rather than to its non-existence. The observed effects of non-equivalence thus are greater if the non-equivalent groups are on P^{III} than on P^{V}. Thus P^{V}

appears to be a more effective chiral centre than P^{III} in causing these non-equivalences. Since a planar environment about the phosphorus would destroy the chirality, it may be that P^{III} is more planar than P^{V} when CF_3 and F substituents are attached and hence less chiral. It must be noted here that planarity of phosphorus to which two CF_3 groups or F atoms are joined will also destroy the non-equivalence if free internal rotations within the molecules are allowed. Thus if the suggestion of greater planarity is to hold, it is necessary that either: (a) trivalent phosphorus tends more towards planarity when one F atom and one CF_3 group are attached than when both substituents are the same, or (b) the effect is for some reason more pronounced if it is the chiral P^{III} atom that is tending to planarity than if P^{III} is bound to the non-equivalent groups.

2. Systematic variations in the nmr parameters of the mixed valence compounds.

Several trends are observed in the nmr parameters of this closely related series of compounds. The short range fluorine to phosphorus coupling constants, $^{1}J_{FP}$ and $^{2}J_{FP}$, are seen (Table 10) to be directly dependent on the nature of the remaining substituents on the same phosphorus atom except in the case of CF_3 on P^{III}. By increasing the trifluoromethyl substitution from 0 to 1 a drop of $^{1}J_{FP}$ from

TABLE 10

Collected Nmr Coupling Parameters for the Series of Mixed Valence Compounds

Compound	Substituents on P^{III}	Substituents on P^{V}	$^{1}J_{FP}$ P^{III}	$^{1}J_{FP}$ P^{V}	$^{2}J_{FP}$ P^{III}	$^{2}J_{FP}$ P^{V}	J_{FF}^{gem} P^{III}	J_{FF}^{gem} P^{V}
I	F,F	F,F	1323.6	1209.9				
II	CF_3,CF_3	CF_3,CF_3	-	-	81.3	111.7		
III	CF_3,CF_3	F,F	-	1223	78	-		
IV	F,F	CF_3,F	1131	-	-	113	-	-
V	CF_3,CF_3	CF_3,F	-	1173.4	78.5	134.5	9.0	3.0
VI	F,F	CF_3,F	1370.0 1291.0	1174.0	-	136.0	92.5	2.6
VII	CF_3,F	CF_3,CF_3	1161.2	-	77.8	112.5	3.4	7.2
VIII	CF_3,F	F,F	1154.0	1124 1203	72.6	-	4.2	82.5
IX	CF_3,F	CF_3,F	1156	1165	74	134	5.0	2.8
X	CF_3,F	F,CF_3	1148	1180	75	134	4.3	2.8

about 1330 Hz to about 1155 Hz for fluorine bound to P^{III} results (Table 11). Similarly fluorine on P^{V} in the difluorinated compounds shows $^{1}J_{FP}$ of about 1215 Hz, while compounds with only a single fluorine atom attached to P^{V} have couplings of about 1175 Hz (Table 11). It is possible to rationalize this behaviour if the existence of F-P π type interactions are allowed. Thus the following resonance structures may be postulated.

It is reasonable to expect that if this donation of π electrons from fluorine to phosphorus does occur, a synergic donation of σ electrons from phosphorus to fluorine will also be observed. This effect should be more pronounced for compounds with two fluorine atoms joined to P^{III} than those with a fluorine atom and a trifluoromethyl group due to the greater stability of the more delocalized π system.[71] Also the greater electronegativity of two fluorine atoms as compared to only one fluorine and a trifluoromethyl group [4] will result in a greater purely inductive withdrawal of σ electrons into the P-F bonds. Since the generally acknowledged origin of nmr coupling constants arises from the existence of electrons with finite probabil-

TABLE 11

Averaged Nmr Parameters for the Series of Mixed Valence Compounds

Grouping	Compounds	$^1J_{FP}$	$^2J_{PP}$	$^3J_{PP}$	ϕ_F	ϕ_{CF_3}	ϕ_P
F_2P [b]	I,IV,VI	1329 ± 5 [a]	-	68 ± 5	59 ± 4	-	-79 ± 2
$CF_3(F)P$	VII,VIII,IX,X	1155 ± 7	75 ± 3	97 ± 11	166 ± 2	63 ± 1	-37 ± 3
$(CF_3)_2P$	II,III,V	-	79 ± 2	100 ± 4	-	54 ± 1	$+103 \pm 6$
$F_2P(S)$ [b]	I,III,VIII	1215 ± 8	-	-	16 ± 2	-	$+38 \pm 6$
$CF_3(F)P(S)$	V,VI,IX,X	1173 ± 8	135 ± 1	-	58 ± 5	76 ± 4	$+33 \pm 6$
$(CF_3)_2P(S)$	II,IV,VII	-	112 ± 1	-	-	69 ± 2	$+71 \pm 9$

a) Maximum deviation from the average of these values for all compounds possessing the particular group

b) Non-equivalent $^1J_{FP}$ averaged for purpose of deviations

ties at the nucleus, (i.e. 's' electron density) [70] it follows that $^1J_{FP}$ should be bigger in the F_2P moiety than in $CF_3(F)P$ as is observed. It was also shown that this effect is larger for P^{III} substituents than for P^V substituents. This may be a reflection of the greater availability of the lone pair of electrons on the trivalent phosphorus atom, which are in a σ-type orbital and which are available for synergic back donation, and inductive withdrawal than the σ electrons on the pentavalent phosphorus atoms which are involved in the phosphorus sulfur double bond.

These arguments may also be used to rationalize the decrease in $^2J_{FP}$ when the trifluoromethyl substitution is increased from 1 to 2 on P^V (Tables 10 and 11) although it is not clear why the effect is essentially non-existent on P^{III}. Here it would be expected that the greater total electronegativity of the $CF_3(F)$ grouping should result in a greater inductive withdrawal of σ electrons than in the case of $(CF_3)_2$ and hence a larger value of $^2J_{FP}$. Since the magnitude of $^1J_{FP}$ was observed to decrease much more dramatically with increasing the CF_3 substitution for the trivalent phosphorus cases as compared to their pentavalent analogs, it may be that more resonance stabilization is lost in the former case than in the latter. Thus the single fluorine on P^{III} may actually inductively withdraw σ electrons from the CF_3-P bond or at least more effectively

compete for them as compared to the P^V case thus negating the greater total electronegativity of the grouping of substituents on phosphorus in the P^{III} case.

Although the chemical shift of the trifluoromethyl groups in these compounds is relatively insensitive to changes in the degree of CF_3 substitution, (Tables 11 and 12) the chemical shifts of fluorine atoms bound directly to phosphorus change significantly with substitution at P^{III} or P^V. In both cases, the chemical shift of the directly bound fluorine increases on raising the CF_3 substitution from 0 to 1, with the trivalent cases showing the most dramatic changes. This may be due to decreased π interactions in compounds with $CF_3(F)P$ substitution as compared with F_2P groupings resulting in higher shielding and hence larger chemical shifts in the former case. At the same time, the phosphorus chemical shift increases from about -79 ppm for difluorinated trivalent phosphorus to -37 ppm for $CF_3(F)P$ substitution to approximately +103 ppm for the $(CF_3)_2P$ grouping. The pentavalent phosphorus atoms show increases in shift from about +35 ppm for the first two cases to +71 ppm for compounds with two CF_3 groups attached (Table 11). Although the π donation from fluorine to phosphorus would be expected to decrease with increasing CF_3 substitution and result in less shielding and lower shifts, the reverse order is observed. This suggests that the inductive effect which diminishes in

TABLE 12

Collected Chemical Shift Parameters for the Series of Mixed Valence Compounds

Compound	Substituents on P^{III}	Substituents on P^{V}	$\phi_F(III)^a$	$\phi_F(V)^a$	$\phi_{CF_3}(III)^a$	$\phi_{CF_3}(V)^a$	$\phi_P(III)^b$	$\phi_P(V)^b$
I	F,F	F,F	60.8	14.4	-	-	-78	38.2
II	CF_3,CF_3	CF_3,CF_3	-	-	53.8	68.7	106.0	65.2
III	CF_3,CF_3	F,F	-	17.9	55.0	-	107.2	42.1
IV	F,F	CF_3,CF_3	61.2	-	-	71.2	- 81.4	80.5
V	CF_3,CF_3	CF_3,F	-	59.2	54.2	74.0	96.8	31.4
VI	F,F	CF_3,F	55.3 (49.4)	53.3 (47.4)	-	80.1 (74.2)	-76.5	39.0
VII	CF_3,F	CF_3,CF_3	164.7 (158.8)	-	62.0 (56.1)	68.5 (62.6)	-34.6	67.3
VIII	CF_3,F	F,F	167.1 (161.2)	16.1 (10.2)	64.1 (58.2)	-	- 37.2	31.3
IX	CF_3,F	CF_3,F	164.8 (158.9)	59.1 (53.2)	63.6 (57.7)	74.1 (68.2)	- 38	28.6
X	CF_3,F	F,CF_3	166.4 (160.5)	58.9 (53.0)	63.6 (57.7)	74.5 (68.6)	- 38	30.6

a) ^{19}F chemical shifts given relative to $CFCl_3$. Bracketed values relative to CF_2Cl_2.

b) ^{31}P chemical shifts measured relative to P_4O_6.

going from F_2P to $CF_3(F)P$ to $(CF_3)_2P$, and which would result in greater σ electron density on phosphorus and hence higher shielding, is a more important effect. Although the changes in fluorine chemical shift are rationalized on the basis of π interactions while those on phosphorus seem to depend on σ effects, it may be noted that changes of electron density in the former case originate in the 2p fluorine orbitals. These are probably much more effective for shielding than the more diffuse 3d orbitals [72] on phosphorus which would be involved in the postulated π interactions and the phosphorus 3s and 3p orbitals involved in σ bonding are likely more important for shielding this nucleus.

The observed decrease in $^2J_{PP}$ from about 100 Hz for compounds in which the trivalent phosphorus is joined to two CF_3 groups or one CF_3 group and one fluorine atom to approximately 68 Hz for compounds with difluorinated trivalent phosphorus (Table 13) may also be accounted for by these arguments. For the latter cases where the synergic back donation of electrons is thought to be the greatest, this may result in withdrawal of σ electrons from the P-S-P system thus lowering $^2J_{PP}$.

Attempts have been made to rationalize the nmr coupling and chemical shift parameters for a large series of phosphine, phosphoryl, and thiophosphoryl compounds containing fluorine atoms and for trifluoromethyl groups by similar

TABLE 13

Collected Nmr Coupling Parameters for the Series of Mixed Valence Compounds

$^{4}J_{FP}$, $^{3}J_{FP}$, and $^{2}J_{PP}$

Compound	Substituents on		$^{4}J_{FP}$		$^{3}J_{FP}$		$^{2}J_{PP}$
	P^{III}	P^{V}	CF_3 on P^{III}	CF_3 on P^{V}	F on P^{III}	F on P^{V}	
I	F,F	F,F	-	-	22.5	14.3	67.8
II	CF_3,CF_3	CF_3,CF_3	0.6	4.9	-	-	103.0
III	CF_3,CF_3	F,F	n.o.	-	-	2	96.5
IV	F,F	CF_3,CF_3	-	1.8	18	-	73
V	CF_3,CF_3	CF_3,F	0.0	7.0	-	10.5	100.0
VI	F,F	CF_3,F	-	0.0	9.0 23.0	22.0	63.0
VII	CF_3,F	CF_3,CF_3	0.0	6.0 2.5	3.8	-	92.4
VIII	CF_3,F	F,F	0.0	-	1.2	0.5 16.3	104.7
IX (major)	CF_3,F	CF_3,F	0.0	5.2	5	n.r.	86
X (minor)	CF_3,F	F,CF_3	0.0	2.8	4	n.r.	103

arguments.[16a] These have met with some success and, although not completely reliable, such descriptions appear to have some predictive value.

One further observation for which no detailed explanation is offered is the larger magnitude of the four bond trifluoromethyl to distant phosphorus coupling when CF_3 is joined to P^V than the corresponding coupling when the CF_3 is bound to P^{III}. This follows the same order as $^2J_{FP}$ which is larger for CF_3 on P^V than for CF_3 on P^{III}. No such behaviour is observed for $^3J_{FP}$ as is seen in Table 13.

3. <u>The ^{31}P nmr spectrum of trivalent phosphorus in $F_2P(S)SP(F)CF_3$ (VIII)</u>

An apparent anomaly was observed in the ^{31}P spectrum of $F_2P(S)SP(F)CF_3$ (VIII). The spectrum arising from the trivalent phosphorus atom shows a doublet of doublets of quartets of doublets whose origin is shown in Figure 11. Half of the lines in half of the large doublet are further split by approximately 2.5 Hz into doublets. Since there is still a single fluorine which is apparently uncoupled, the splitting may arise from interaction with it. This however should split all the lines equally. A more likely explanation is that in fact a spin tickling phenomenon[14] is being observed as a result of the proximity of half of the fluorine doublet from one of the fluorine atoms bound

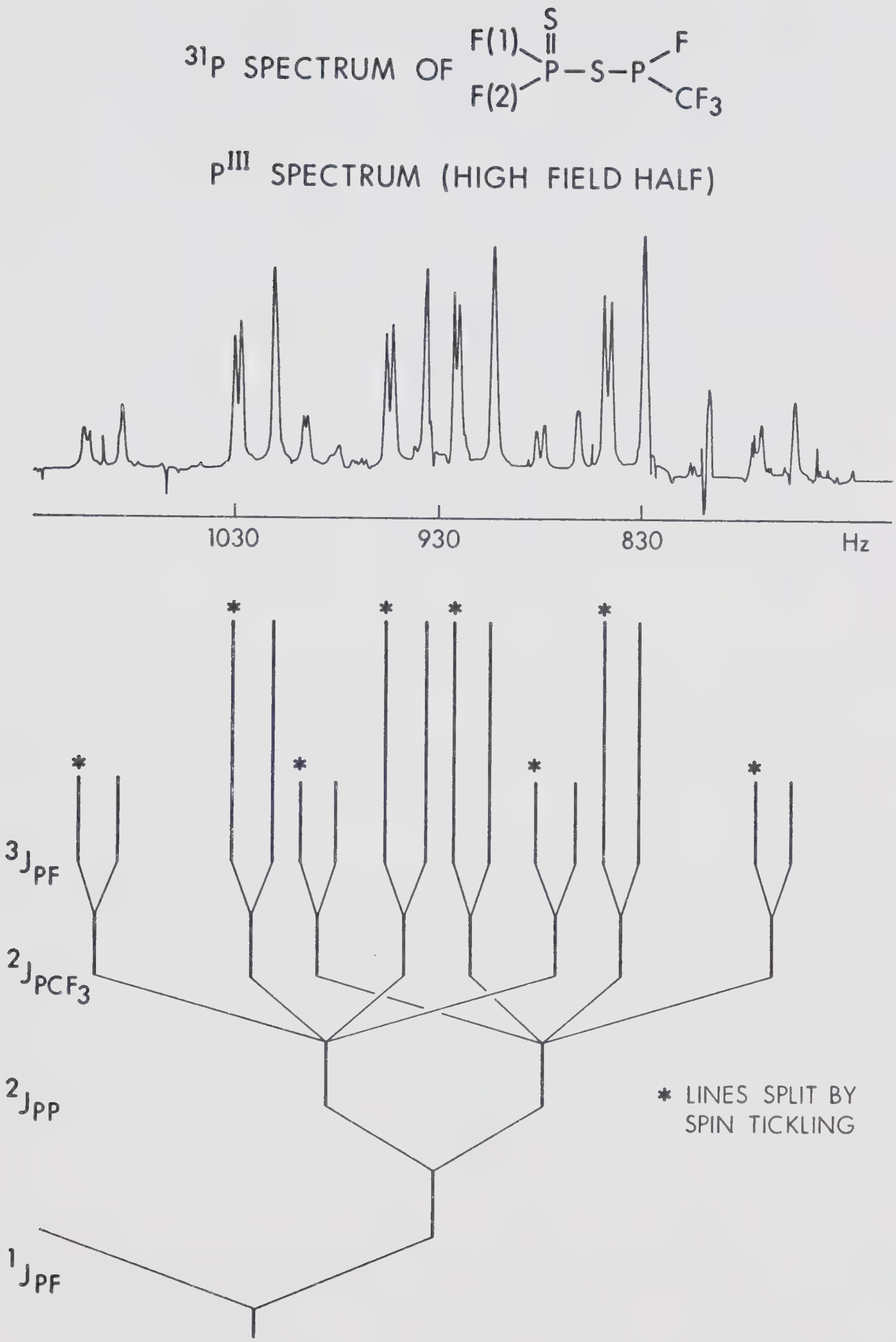


FIGURE 11 High field half of ^{31}P spectrum of P^{III} in $F_2P(S)SP(F)CF_3$. Asterisks denote lines which split by spin tickling.

to P^V to the signal from the solvent (CF_2Cl_2) which served as the spectrometer lock signal. Irradiation of the sample at this lock frequency not only involves nmr transitions in the solvent but will also be in resonance with certain transitions of compound VIII. Thus a double resonance experiment is in effect being performed and one group of lines from the fluorine atoms bound to P^V will be spectroscopically pumped. Since lines arising from coupling of P^{III} to P^V and to CF_3 are all affected equally, transitions of these nuclei need not be considered in order to rationalize the observed spectra. The fluorine atom on P^V which is not coupled to P^{III} may also be omitted in explaining this effect. Thus the nuclei which are important to this phenomenon are P^{III}, whose spectrum is being observed, F on P^{III}, since only half of the lines resulting from coupling of these species are affected, and the fluorine atom on P^V which is coupled to P^{III} since its transitions are being affected by the lock frequency. Figure 12 is the nuclear energy level diagram,[73] resulting from these nuclei whose labels represent the spin of P^{III}, F on P^{III}, and F on P^V respectively. The solid arrowheads represent transitions of the fluorine atom on P^V which can be "tickled" or "pumped" and the open arrowheads are the possible nmr transitions of P^{III}. It may be seen that if only one of the fluorine transitions is pumped, that being the one closest the lock frequency, two of the

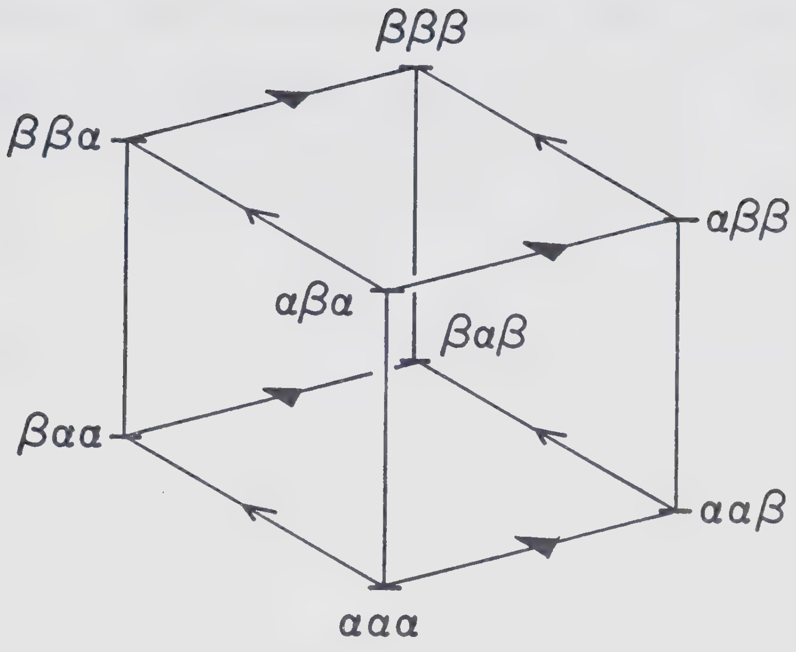


FIGURE 12 Partial energy level diagram of $F_2P(S)SP(F)CF_3$ showing some allowed nmr transitions.

phosphorus lines will be affected. Freeman and Anderson have shown [73] that the first change from this phenomenon is splitting of one of these lines and enhancement of the intensity of the other. The other two transitions which form the other half of the doublet due to coupling of F on P^{III} to P^{III} should be unaffected as is apparently the case (see Figure 8). Although intensity changes of half of the lines are rather difficult to discern, it is clearly seen in Figure 11 that half of the remaining lines are split into doublets and that these are half of the lines which arise from coupling to F on P^{V}. Thus it

appears that the observed results may be explained by this spin tickling phenomenon.

CHAPTER 5

REACTIONS OF COMPOUNDS CONTAINING P-P BONDS WITH CF_3I AND CH_3I AND RELATED CHEMISTRY

INTRODUCTION

The traditional starting point for the synthesis of trifluoromethyl substituted phosphorus compounds has been to make $(CF_3)_nPI_{3-n}$ (n = 0,1,2,3) from the reaction of CF_3I with elemental phosphorus.[3] Addition of elemental iodine to the reaction mixture reduces the yield of $(CF_3)_3P$ and increases the amounts of the iodo phosphines obtained.[3] Since most investigations of trifluoromethylated phosphorus compounds have required the use of only one of the phosphines produced by this reaction, a facile way of adding or removing CF_3 groups from phosphorus to optimize the yield of the appropriate compound would be highly desirable. Hydrolysis reactions are known to remove these groupings as fluoroform, but unfortunately also substitute oxygen in their place which is even more difficult to displace. A more convenient method of reducing the CF_3 substitution from three to two has been reported for $(CF_3)_3P$ [74] and $(CF_3)_3PO$.[75] This involves reaction of dimethylamine with the trisubstituted compounds to give $(CF_3)_2PN(CH_3)_2$ or $(CF_3)_2P(O)N(CH_3)_2$ respectively. While the latter reaction is quantitative and rapid at room temperature, the former gives low yields of the aminophosphine and then only at

elevated temperatures. This reaction can be driven to completion by the addition of H_2S to the reaction mixture.[63] Thus the initially formed dimethylaminophosphine is consumed to yield an adduct which can be formulated as the dimethylammonium salt of $(CF_3)_2PS^-$.

Reduction of the CF_3 substitution from two to one is also possible. Dimethylamine has been shown to react with $(CF_3)_2POSi(CH_3)_3$ to give $CF_3P(N(CH_3)_2)OSi(CH_3)_3$ [76] but the synthetic possibilities of this reaction have not yet been fully explored since it is not known how easily the $OSi(CH_3)_3$ grouping can be removed. In this Chapter we compare the facile reaction of $(CF_3)_3PO$ with dimethylamine with the analogous reaction of $(CF_3)_3PS$.

Methods of increasing the trifluoromethyl substitution on arsines were studied in some detail by Cullen, who found that tetrakis(trifluoromethyl)diarsine, $(CF_3)_2AsAs(CF_3)_2$, reacted with CF_3I to give $(CF_3)_3$ As and $(CF_3)_2AsI$ [24] and with CH_3I to give $(CF_3)_2AsCH_3$ in much poorer yield. Addition of mercury to the latter reaction increased the yield to about 10%. Similar reactions were observed with the analogous diphosphine, $(CF_3)_2PP(CF_3)_2$ [24] but mercury was used only to remove the $(CF_3)_2PI$ from the product mixture. Further studies showed that $(CH_3)_2AsI$ [24], CH_3AsI_2 [24] and several phenyl substituted iodoarsines [77] all reacted with CF_3I and mercury to give trifluoromethylated arsines in varying yields. A similar method has been used in the synthesis

of $CF_3(CH_3)PX$.[56] A mixture of $(CF_3P)_4$ and $(CF_3P)_5$, cyclic phosphines prepared from the reaction of CF_3PI_2 [26,27] and mercury, was reacted with CH_3I to give $CF_3(CH_3)PI$.[56] A recent method of increasing the CF_3 substitution from zero to one involves displacement of one of the dimethylamine groups in tris(dimethylamino)phosphine by CF_3I at 60°C.[78] A second CF_3 group could not be substituted.

Several experiments aimed at improving the yields of CF_3I and CH_3I additions to compounds having phosphorus-phosphorus bonds are reported in this Chapter. Some chemical studies on $(CF_3)_2PCH_3$, one of the products of these reactions, have led to the identification of several new compounds. The hydrolysis reactions of several compounds are also included in this Chapter.

EXPERIMENTAL

1. Reactions of CF_3I

(a) With $(CF_3P)_{4,5}$ and mercury

A mixture of $(CF_3P)_{4,5}$ (0.2647 gm; 2.65 mmole of CF_3P) and CF_3I (1.0379 gm; 5.29 mmole) was shaken for four days with excess mercury. Fractionation of the volatile products yielded unreacted CF_3I (0.066 gm; 0.34 mmole) and $(CF_3)_3P$ (0.6006 gm; 2.52 mmole) (95%).

(b) With $(CF_3)_2PP(CF_3)_2$ and mercury

Warming (70°C) and shaking a mixture of $(CF_3)_4P_2$ (0.5546 gm; 1.64 mmole) and CF_3I (0.6634 gm; 3.38 mmole) for three days with excess mercury gave unreacted CF_3I (0.0299 gm; 0.15 mmole) and $(CF_3)_3P$ (0.7257 gm; 3.05 mmole) (93%).

(c) With P_2I_4 and mercury

A mixture of P_2I_4 (0.7 gm; 1 mmole) and CF_3I (0.6640 gm; 3.39 mmole) was heated at 150°C with excess mercury. After four days, the only volatile product was unreacted CF_3I (0.6083 gm; 3.10 mmole) containing a trace of $(CF_3)_3P$.

(d) With P_2I_4

A large excess of CF_3I and P_2I_4 (0.7 gm; 1 mmole) were heated for two days at 200°C. Fractionation of the volatile products yielded only a small amount of trifluoromethyl substituted products and unreacted CF_3I.

2. Reactions of CH_3I

(a) With $(CF_3P)_{4,5}$ and mercury

Shaking a mixture of $(CF_3P)_{4,5}$ (0.545 gm; 5.45 mmole of CF_3P) and CH_3I (1.5448 gm; 10.88 mmole) with excess mercury for two days gave 0.2174 gm of a mixture of $(CF_3)_3P$ (16%), $(CF_3)_2PCH_3$ (84%) and a trace of what is probably $CF_3P(CH_3)_2$ as volatile products. As well, large amounts of green solid remained in the reaction vessel.

(b) With $(CF_3)_2PP(CF_3)_2$ and mercury

After reacting for three days at 150°C, a mixture of $(CF_3)_4P_2$ (0.3783 gm; 1.12 mmole) and CH_3I (0.3574 gm; 2.52 mmole) and excess mercury gave as volatile products unreacted CH_3I (0.0041 gm; 0.02 mmole) and $(CF_3)_2PCH_3$ (0.4067 gm; 2.21 mmole) containing small amounts of $(CF_3)_3P$ and probably $CF_3P(CH_3)_2$.

The ^{19}F nmr spectrum of a solution of $(CF_3)_2PCH_3$ in $CFCl_3$ showed a doublet of quartets (ϕ_F = 58.2 ppm, $^2J_{FP}$ = 76.2 Hz, $^4J_{FH}$ = 0.2 Hz) while the ^1H spectrum consisted of a doublet (τ 8.43, $^2J_{HP}$ = 4.5 Hz) with an unresolved proton to fluorine coupling. The nmr spectral parameters for the material thought to be $(CF_3)P(CH_3)_2$ were: ϕ_F = 65.1, $^2J_{FP}$ = 65 Hz, τ 8.75, $^2J_{HP}$ = 3.3 Hz.

The mass spectrum of $(CF_3)_2PCH_3$ showed a parent ion peak (Found: m/e = 183.9860, calc. for $C_3H_3F_6P$: m/e = 183.9860). All other peaks were assignable to fragmentation

products of $(CF_3)_2PCH_3$ and no peak corresponding to m/e 130 for $CF_3P(CH_3)_2$ was detected.

(c) With $(CF_3)_2PP(CF_3)_2$

After two days at 150°C a mixture of $(CF_3)_4P_2$ (0.2335 gm; 0.69 mmole) and CH_3I (0.1005 gm; 0.708 mmole) gave a inseparable mixture of CH_3I, $(CF_3)_2PI$ and $(CF_3)_2PCH_3$.

3. Reactions of $(CF_3)_2PCH_3$

(a) With sulfur

Heating $(CF_3)_2PCH_3$ (0.404 gm, 2.19 mmole) with excess sulfur for three days at 150°C gave a mixture of $(CF_3)_2P(S)CH_3$ and $(CF_3)_2PCH_3$ (0.2965 gm) as the only volatile products. Repeated fractionations yielded pure $(CF_3)_2P(S)CH_3$ (0.1381 gm; 0.64 mmole) and a mixture containing principally $(CF_3)_2PCH_3$ with some $(CF_3)_2P(S)CH_3$ (0.1584 gm by difference).

The ^{19} nmr spectrum of a solution of $(CF_3)_2P(S)CH_3$ in $CFCl_3$ showed a doublet of quartets (ϕ_F = 71.2 ppm, $^2J_{FP}$ = 96.9 Hz, $^4J_{FH}$ = 0.8 Hz) while the ^1H spectrum consisted of a doublet of septets (τ 7.82; $^2J_{HP}$ = 14.85 Hz; $^4J_{HF}$ = 0.8 Hz).

The mass spectrum of $(CF_3)_2P(S)CH_3$ showed a parent ion peak (Found m/e = 215.9594; calc. for $C_3H_3F_6PS$: m/e = 215.9597).

(b) With dimethylamine

After twelve days at 195°C, dimethylamine (0.1376 gm; 3.06 mmole) displaced a small amount of CF_3H from $(CF_3)_2PCH_3$ (0.2702 gm; 1.47 mmole) to give a mixture of unreacted starting materials (0.3908 gm) and a trace of material thought to be $CF_3P(CH_3)N(CH_3)_2$ (0.0072 gm) characterized only by infrared spectroscopy.

(c) With chlorine

A mixture of $(CF_3)_2PCH_3$ (0.2082 gm; 1.11 mmole) and chlorine (0.0792 gm; 1.12 mmole) was allowed to warm slowly to room temperature. The crude reaction product was found to contain $(CF_3)_2PCH_3$ (10%) and $(CF_3)_2P(CH_3)Cl_2$ (90%). After fractionation pure $(CF_3)_2P(CH_3)Cl_2$ (0.2363 gm; 0.925 mmole) was obtained whose nmr parameters were determined (ϕ_F = 79.7 ppm; $^2J_{FP}$ = 134 Hz; τ 7.94; $^2J_{HP}$ = 11 Hz).

(d) Alkaline hydrolysis

A sample of $(CF_3)_2PCH_3$ (0.1459 gm; 0.793 mmole) was combined with an excess of a 20% solution of NaOH in water and shaken for 12 hours at 25°C. The reaction had not gone to completion under these conditions so the mixture was recombined and heated for 4 days at 70°C. The only volatile product was CF_3H (0.1098 gm; 1.569 mmole: required for hydrolysis of two CF_3 groups = 1.586 mmole).

The aqueous solution was analysed by nmr spectroscopy and found to contain the $CH_3(H)PO_2^-$ anion ($^2J_{HP}$ = 14.5 Hz

$^{1}J_{HP}$ = 523 Hz; $^{3}J_{HH}$ = 2 Hz; τ_{CH_3} 8.34; τ_H 2.5) but there were no ^{19}F resonances.

(e) With water

A mixture consisting of $(CF_3)_2PCH_3$ (0.1447 gm; 0.786 mmole) and an excess of water was shaken at 25°C for 12 hours and then heated at 70°C for 4 days. The volatile product was found to be only unreacted $(CF_3)_2PCH_3$ (0.1420 gm; 0.772 mmole).

4. Reactions of $(CF_3)_2P(S)CH_3$

(a) Alkaline hydrolysis

A mixture of $(CF_3)_2P(S)CH_3$ (0.2397 gm; 1.11 mmole) and an excess of a 20% solution of NaOH in water was heated at 70°C for ten days. The volatile product was found to be pure CF_3H (0.1528 gm; 2.19 mmole: required for 2 CF_3 groups = 2.22 mmole). The aqueous solution was analysed by nmr spectroscopy and found to have a ^{1}H spectrum consisting of two singlets (τ 8; τ 8.2). The ^{19}F nmr spectrum contained no signals.

(b) With water

A mixture of $(CF_3)_2P(S)CH_3$ (0.2326 gm; 1.08 mmole) and an excess of water was heated for 10 days at 70°C. The volatile products were found to be a mixture (0.1093 gm) of CF_3H and H_2S by infrared spectroscopy. Removal of the H_2S with a $Pb(OAc)_2$ solution gave CF_3H (0.074 gm; 1.06 mmole)

as the only volatile product. The amount of H_2S present (0.0353 gm; 1.04 mmole) was determined by difference. The aqueous solution was analyzed by nmr spectroscopy. The ^{1}H spectrum was found to consist of a doublet (J_{HP} = 15.5; τ 8.55) as did the ^{19}F spectrum (J_{FP} = 93, ϕ = 76.8 ppm). These values are consistent with those which would be expected for $CF_3(CH_3)PO_2^-$.

5. <u>Fluorination of $(CF_3)_2P(CH_3)Cl_2$ with SbF_3</u>

Pure $(CF_3)_2P(CH_3)Cl_2$ (0.2363 gm; 0.925 mmole) was combined with an excess of SbF_3 and allowed to react at 25°C for two days in a sealed tube. The volatile products (0.1688 gm) were analyzed by nmr spectroscopy and found to contain $(CF_3)_2P(CH_3)F_2$ (30%) ($^{1}J_{FP}$ = 830 Hz, $^{2}J_{FP}$ = 156 Hz, $^{3}J_{FF}$ = 17 Hz, ϕ_F = 44.6 ppm; ϕ_{CF_3} = 66.5 ppm; $^{2}J_{HP}$ = 18.3 Hz, $^{3}J_{HF}$ = 11.7 Hz; τ 8.25) and $(CF_3)_2P(O)CH_3$ (70%) ($^{2}J_{FP}$ = 100 Hz; ϕ_F = 71.7 ppm, $^{2}J_{HP}$ = 15 Hz, $^{4}J_{HF}$ = 0.7 Hz; τ 8.25).

6. <u>Reaction of $(CF_3)_3PS$ with $(CH_3)_2NH$</u>

A mixture of $(CF_3)_3PS$ (0.2917 gm; 1.04 mmole) and $(CH_3)_2NH$ (0.0447 gm; 0.99 mmole) was reacted for 20 hr at 25°C. Fractionation of the volatile products gave $(CF_3)_2P(S)N(CH_3)_2$ (0.2479 gm; 1.02 mmole) and CF_3H (0.0759 gm; 1.08 mmole).

7. $\underline{\text{Reactions of } (CF_3)_2PSP(CF_3)_2}$

(a) Alkaline hydrolysis

A mixture of $(CF_3)_2PSP(CF_3)_2$ (0.2774 gm; 0.750 mmole) and an excess of a 20% solution of NaOH in water was shaken for 12 hr at 25°C. The only volatile product was CF_3H (0.2087 gm; 2.98 mmole; required for hydrolysis of 4 CF_3 groups = 3.00 mmole). The ^1H nmr spectrum of the aqueous solution consisted of two sets of doublets (J_{HP} = 575 Hz, τ 2.45: J_{HP} = 662.5 Hz; τ 2.45). These are assigned to HPO_3^- and $HP(S)O_2^-$ respectively. The solution gave a positive test for sulfide ion on addition of sodium nitroprusside. There were no ^{19}F nmr resonances.

(b) Neutral hydrolysis

The reaction of $(CF_3)_2PSP(CF_3)_2$ (0.1758 gm; 0.475 mmole) with an excess of water gave CF_3H and H_2S as volatile products (0.1443 gm; required for 4 CF_3 groups and H_2S = 0.1490 gm). The aqueous solution showed no ^{19}F nmr spectrum but had a ^1H resonance which consisted of a simple doublet (J_{HP} = 672.5, τ 3.17) that is consistent with the spectrum expected for H_3PO_3.

(c) Acid hydrolysis

A mixture of $(CF_3)_2PSP(CF_3)_2$ (0.2932 gm; 0.792 mmole) in an excess of a 25% solution of H_2SO_4 in water was heated at 70°C for 10 days. The volatile products (0.1809 gm) were found to be a mixture of CF_3H and H_2S, whose gas phase molecular weight was 65.7. The amounts of the two compounds pre-

sent were calculated from the molecular weight and the total weight of the sample. (CF_3H : 2.38 mmole; H_2S : 0.396 mmole). The ^{19}F nmr spectrum of the aqueous solution consisted of a doublet of doublets (J_{FP} = 106 Hz, J = 4 Hz, ϕ = 77.1 ppm; 45%) and three sets of doublets (J = 93 Hz; ϕ = 72.7 ppm; 39%; J = 82 Hz; ϕ = 72.4 ppm; 9%; J = 90 Hz ϕ = 74.4 ppm; 7%). The ^1H nmr spectrum was a simple doublet (J = 707.5 Hz; τ 2.97).

8. Reactions of $(CF_3)_2POP(CF_3)_2$

(a) Alkaline hydrolysis

A pure sample of $(CF_3)_2POP(CF_3)_2$ (0.2064 gm; 0.584 mmole) was shaken for 12 hr with an excess of a 20% solution of NaOH in water. the only volatile product recovered was CF_3H (0.1624 gm; 2.32 mmole; required for hydrolysis of 4 CF_3 groups = 2.34 mmole). The aqueous solution was found to contain only $HPO_3^{=}$ by nmr spectroscopy ($^1J_{HP}$ = 575.5 Hz; τ 2.78). No ^{19}F resonances were observed.

(b) Neutral hydrolysis

After 4 days at 70°C the hydrolysis of an aqueous solution of $(CF_3)_2POP(CF_3)_2$ (0.1912 gm; 0.540 mmole) was incomplete. Further heating for 7 days gave CF_3H (0.1469 gm; 2.10 mmole: required for hydrolysis of 4 CF_3 groups = 2.16 mmole) as the only volatile product. The ^1H nmr spectrum of the aqueous solution indicated the presence of only

H_3PO_3 ($^1J_{HP}$ = 674 Hz; τ 3.1). No ^{19}F nmr signals were observed.

(c) Acid hydrolysis

After 50 days at 25°C, a solution of $(CF_3)_2POP(CF_3)_2$ (0.2420 gm; 0.684 mmole) in 25% aqueous H_2SO_4 gave CF_3H (0.1276 gm; 1.825 mmole) as the only volatile product. An off-white to yellow colored solid was also formed which had the physical appearance of elemental sulfur. It was soluble in CS_2 and melted at 115°C (rhombic S m.p. 112.8; monoclinic S m.p. 119). The ^1H nmr spectrum of the aqueous hydrolysate consisted of a doublet ($^1J_{HP}$ = 719 Hz; τ 2.83). The ^{19}F nmr spectrum was also a doublet ($^2J_{FP}$ = 115 Hz; ϕ_F = 74.3 ppm).

RESULTS AND DISCUSSION

The previously observed reactions of dimethylamine with $(CF_3)_3P$ [74] and $(CF_3)_3PO$ [75] which eliminated one equivalent of fluoroform and gave the appropriate dimethylamino substituted compound has now been extended to include $(CF_3)_3PS$. All three of these compounds react according to equation 17 with both the oxygen and sulfur substituted

$$(CF_3)_3PE + (CH_3)_2NH \longrightarrow (CF_3)_2P{\genfrac{}{}{0pt}{}{\diagup\!\!\!\!\diagup E}{\diagdown N(CH_3)_2}} + CF_3H \qquad (17)$$

E = O, S, or nothing.

compounds reacting rapidly and quantitatively. This method provides a convenient route to the bis(trifluoromethyl)-phosphoryl and thiophosphoryl compounds and allows the reduction of the CF_3 substitution on phosphorus from three to two.

The early work of Cullen showed that tetrakis(trifluoromethyl)diphosphine reacted with CF_3I to give $(CF_3)_3P$ and $(CF_3)_2PI$.[24] Since it was well known that the latter product is coupled by mercury to give the diphosphine starting material [3], mercury was added to the initial reaction mixture. This resulted in a 93% yield of $(CF_3)_3P$. A slightly higher yield of $(CF_3)_3P$ was obtained when $(CF_3P)_{4,5}$ was shaken with CF_3I and mercury. This allowed the facile expansion of the CF_3 substitution on phosphorus from either one or two to three and suggested the possibility of

an analogous reaction with P_2I_4.[25] Only very small amounts of $(CF_3)_3P$ and no other trifluoromethylated phosphorus compounds were obtained by this method although quite vigorous conditions were employed. Repeating the reaction with no mercury present and at a higher temperature similarly gave only trace amounts of trifluoromethylated phosphines and it is likely that in both experiments decomposition of P_2I_4 to elemental phosphorus and iodine led to the well known addition of CF_3I to phosphorus.[3]

Methyl iodide reacted with $(CF_3)_2PP(CF_3)_2$ in the presence of mercury to give, almost quantitatively, $(CF_3)_2PCH_3$ which was contaminated by small amounts of $(CF_3)_3P$ and $CF_3P(CH_3)_2$. The analogous reaction with $(CF_3P)_{4,5}$ gave only a trace of the expected $CF_3P(CH_3)_2$. The major products, although obtained in low yields, were $(CF_3)_3P$ and $(CF_3)_2PCH_3$. These almost certainly result from disproportionation of the initially formed $CF_3P(CH_3)_2$ and this suggests that the two major products are more thermally stable than the expected one. Subsequent to this investigation it was found that CH_2I_2 reacted with the diphosphine in the presence of mercury to give $(CF_3)_2PCH_2P(CF_3)_2$.[28]

The recently observed reaction of $(CF_3)_3P$ with dimethylamine to give $(CF_3)_2PN(CH_3)_2$ suggested the possibility of such behaviour with $(CF_3)_2PCH_3$. This reaction unfortunately did not occur; however, reaction with sulfur

produced the new species $(CF_3)_2P(S)CH_3$ by analogy with similar reactions of $(CF_3)_2PX$ [10] (X = F, $N(CH_3)_2$, Cl). This new compound was characterized by its nmr spectrum which showed a doublet of quartets in the ^{19}F region (ϕ_F = 71.2 ppm; $^2J_{FP}$ = 96.9 Hz; $^4J_{FH}$ = 0.8 Hz) and a doublet of septets in the ^1H region (τ 7.82; $^2J_{HP}$ = 14.85 Hz; $^4J_{HF}$ = 0.8 Hz), from precise measurement of the parent peak in its mass spectrum (obs. m/e = 215.9594; calc for $C_3H_3F_6P$ = 215.9597) and from its behaviour on alkaline and neutral hydrolysis. Rather surprisingly, the new compound yielded 2 equivalents of fluoroform on alkaline hydrolysis. This would be expected if the central phosphorus atom was trivalent; however, only one equivalent is predicted for pentavalent species if the behaviour of previously reported $(CF_3)_2P(S)X$ compounds is followed.[10] The anionic species which remained in solution were not conclusively identified but their 60 MHz ^1H nmr spectrum was found to consist of two singlets located at τ 7.96 and τ 8.17. These may in fact be a doublet centred at τ 8.06 with coupling 13 Hz half of which is obscured by a singlet at τ 7.96. This doublet would then have nmr parameters consistent with an anion having a methyl group attached to phosphorus. A similar deviation from empirical prediction was observed in the neutral hydrolysis of this compound. Although removal of CF_3 groups was not expected under neutral hydrolysis conditions in keeping with the behaviour

of other $(CF_3)_2P(S)X$ compounds, one equivalent of CF_3H and one equivalent of H_2S were isolated as volatile products. The aqueous solution remaining in the reaction tube contained a species whose nmr parameters were consistent with those expected for $CF_3(CH_3)PO_2^-$.

The nmr parameters of $(CF_3)_2P(S)CH_3$ clearly indicate that $(CF_3)_2P(S)CH_3$ is different from the previously synthesized trivalent isomer $(CF_3)_2PSCH_3$ [41,79] (ϕ_F = 56.7 ppm; $^2J_{FP}$ = 77.8 Hz; τ 7.61; $^3J_{HP}$ = 15.5). The greater than expected yield of CF_3H on hydrolysis of $(CF_3)_2P(S)CH_3$ may be explained by a water catalysed rearrangement to the trivalent form similar to the behaviour previously observed in the attempted synthesis of $(CF_3)_2P(O)H$.[9] The trivalent compound then may hydrolyse in the expected fashion to yield 2 CF_3H equivalents under alkaline conditions and one equivalent under neutral conditions.

The reaction of trifluoromethyl phosphines with halogens results in the formation of five-coordinate phosphoranes.[3,27,80] $(CF_3)_2PCH_3$ reacts quickly and exothermically with chlorine to give $(CF_3)_2P(CH_3)Cl_2$ which was identified from its room temperature nmr parameters (ϕ_F = 79.7 ppm; $^2J_{FP}$ = 134 Hz; τ_H 7.94; $^2J_{HP}$ = 11 Hz). This compound was readily fluorinated by SbF_3 to give $(CF_3)_2P(CH_3)F_2$ [81] ($^1J_{FP}$ = 830 Hz; $^2J_{FP}$ = 156 Hz; $^3J_{FF}$ = 17 Hz, ϕ_F = 44.6 ppm; ϕ_{CF_3} = 66.5 ppm; $^2J_{HP}$ = 18.3 Hz; $^3J_{HF}$ = 11.7 Hz; τ_H 8.25). As

well, due to traces of moisture in the fluorinating agent, $(CF_3)_2P(O)CH_3$ was formed. The dichloro compound is under study at this time in an attempt to analyse its low temperature nmr spectra which may show the results of slowing the rate of pseudorotational exchange [53] which may average the equatorial and axial coordination sites in these trigonal bipyramidal molecules.

An example of the hindering effect of electropositive groups on the rate of hydrolysis of trifluoromethylated phosphines is given by $(CF_3)_2PCH_3$ which had to be heated at 70°C for 4 days to drive the reaction in 20% aqueous NaOH to completion. This behaviour is different from that of the two diphosphorus compounds containing P^{III}, $(CF_3)_2POP(CF_3)_2$ [33] and $(CF_3)_2PSP(CF_3)_2$ [32] which reacted immediately on contact with the alkaline solution. The methyl substituted phosphine did, however, give a quantitative yield of fluoroform with both trifluoromethyl groups being removed, similar to the behaviour of $(CF_3)_2P(S)CH_3$. The phosphorus containing anion which remained in solution gave an nmr spectrum consistent with that expected for $CH_3(H)PO_2^-$. The compound, $(CF_3)_2PCH_3$, which was expected to lose one CF_3 moiety on neutral hydrolysis was unaffected after 4 days at 70°C.

Both $(CF_3)_2PSP(CF_3)_2$ and $(CF_3)_2POP(CF_3)_2$ evolved 4 equivalents of fluoroform on alkaline hydrolysis. The aqueous solution remaining after hydrolysis of the former

compound showed the presence of sulfide ion as determined by the sodium nitroprusside test as well as HPO_3^- and $HPSO_2^-$ as determined by nmr spectroscopy. The oxygen bridged compound gave only HPO_3^- in the hydrolysate. The identification of these anions by this method is open to some criticism since an authentic sample of H_3PO_3 showed large variations in both coupling and chemical shift parameters of the proton bound directly to phosphorus as the pH was varied. This would presumably be true for the $HPSO_2^-$ anion as well.

Neutral hydrolysis gave, rather unexpectedly, 4 equivalents of fluoroform and 1 equivalent of H_2S from one mole of $(CF_3)_2PSP(CF_3)_2$ and 4 equivalents of fluoroform from one mole of $(CF_3)_2POP(CF_3)_2$. The only anionic species remaining in either solution was identified as H_3PO_3. The sulfur bridged compound yielded 3 equivalents of CF_3H and 0.5 equivalent of H_2S on hydrolysis by an aqueous solution acidified with H_2SO_4. The nmr spectrum of the hydrolysate did not permit identification of any phosphorus containing species present but did indicate that one of them contained a CF_3 group bound to phosphorus. The oxygen bridged compound on acid hydrolysis gave less than 3 equivalents of fluoroform although allowed to react for an extended period. The phosphorus containing species remaining in solution were not identified but the nmr spectrum again indicates the presence of a species containing CF_3 bound to phosphorus

with different parameters to those obtained from $(CF_3)_2PSP(CF_3)_2$ hydrolysis. A totally unexpected product of this reaction was elemental sulfur, identified from its solubility in CS_2 and its melting point, which could only result from reduction of the sulfuric acid present. It is clear that the acid hydrolysis of the two diphosphorus compounds and especially the oxygen bridged species must proceed by very complicated routes.

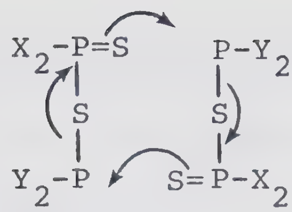
CHAPTER 6

CONCLUSIONS

The original goals of the work described in this thesis were twofold: (1) to elucidate the exchange mechanism involved in the so-called mixed valence compounds, and (2) to develop a better synthesis of the trifluoromethylphosphine starting materials.

The first of these aims has been partially fulfilled and several questions have been answered. It has been shown that an intermolecular exchange process is important in analysing the nmr spectra of $(CF_3)_2P(S)SPF_2$ and that while its rate may vary, it occurs in $(CF_3)_2P(S)SP(CF_3)_2$, $F_2P(S)SP(CF_3)_2$ and $F_2P(S)SPF_2$ as well. Although not explicitly proven, it is likely that this type of exchange occurs in the remaining members of the series as well as systems of the type $[X_2P(E)]_2Y$ where X = F, CF_3; E = S, nothing; Y = S, O, S-S.[80] A near thermoneutral exchange process between the four mixed valence compounds shown above has been determined, with an equilibrium constant of about 1.

An nmr lineshape study is qualitatively consistent with an intermolecular exchange process similar to the one shown below, where the valence of all phosphorus atoms remains unchanged. The molecularity of such a process has not been established. Intramolecular rotational averaging has not been ruled out as a mechanism complementary to the



intermolecular one and may in fact play a role in the observation of very long range spin-spin couplings across the molecule but such processes are thought to contribute little to the nmr spectral behaviour.

The chemistry of the mixed valence compounds is dominated by initial cleavage of the P^{III}-S bond followed in some cases by decomposition or further reaction of the products. The reaction of dimethylamine with all of the compounds has been shown to be quantitative and has proven to be a useful tool in their characterization.

The synthesis of the new dithiophosphinic acid, $CF_3(F)PS_2H$ has opened the door to the synthesis of several other mixed valence compounds and the asymmetric phosphorus centre which is present in these compounds has allowed the measurement of geminal CF_3-CF_3 and F-F nmr coupling constants on trivalent phosphorus. Similarly, chirality in the trivalent species $(CF_3)(F)P$-X, which can be observed as a result of a slow rate of inversion of phosphorus, has allowed measurement of the corresponding geminal couplings between species bound to a pentavalent phosphorus atom. Full analysis of the nmr spectra of all of these molecules has been achieved and the variation of their nmr coupling and

chemical shift parameters with varying substitution of the phosphorus atoms has been rationalized on the basis of differences in electronegativity and π bonding capability of F and CF_3.

Two chiral centres in one mixed valence compound were obtained with the synthesis of $CF_3(F)P(S)SP(F)CF_3$ and the compound was found to exist as an unseparated mixture of two racemates which could be distinguished by nmr spectroscopy. Full analysis of the nmr spectra of this compound has not been possible due to the large number of overlapping lines present in the spectra. It may be possible, however, to solve these spectra by the use of heteronuclear decoupling techniques.

The stability of the compounds studied herein appears to follow the degree of fluorine substitution. As a general rule, the greater the fluorine substitution on phosphorus, the lower the thermal stability. In the mixed valence compounds, when equal numbers of fluorine atoms are present, the compounds with the fewest fluorine atoms bound to trivalent phosphorus are the more stable ones. Thus $F_2P(S)SP(CF_3)_2$ is much more thermally stable than its isomer $(CF_3)_2P(S)SPF_2$ and $CF_3(F)P(S)SP(CF_3)_2$ appears not to decompose at room temperature whereas $(CF_3)_2P(S)SP(F)CF_3$ can only be preserved in the cold. It also appears that fine structure in the nmr spectra is observed at higher temperatures for the more stable isomers.

Future work on these systems might encompass a more concerted attempt to make either one or both of the isomers of $CF_3(F)PSH$. The mixed valence compounds containing oxygen rather than sulfur may provide information about the importance of d-orbitals in the bonding scheme for these compounds since oxygen should not have d-orbitals of low enough energy to participate in bonding. The reported instability of $F_2P(O)OPF_2$ [21] and $(CF_3)_2P(O)OP(CF_3)_2$ [82] as compared to their sulfur analogues seems to indicate that the mixed valence systems do rely on d-orbital interactions and that the oxygen analogs of the compounds reported in this thesis may indeed by very difficult to work with.

While the second of the original aims has not been achieved, it is believed that some systematization has been observed in the reactions of substituted methyl iodides with compounds having phosphorus-phosphorus linkages. It is now possible to increase the trifluoromethyl substitution on phosphorus from one or two to three via the following reaction sequences:

$$CF_3PI_2 + Hg \longrightarrow (CF_3P)_{4,5} \xrightarrow[Hg]{CF_3I} (CF_3)_3P \qquad (18)$$

$$(CF_3)_2PI + Hg \longrightarrow (CF_3)_2PP(CF_3)_2 \xrightarrow[Hg]{CF_3I} (CF_3)_3P \qquad (19)$$

A convenient synthesis of $(CF_3)_2PCH_3$ has also emerged from this method using the second sequence but substituting

CH_3I for CF_3I. Subsequent to this investigation, it was found that the diphosphine underwent a similar reaction with CH_2I_2 to yield a methylene bridged species. The reduction of the CF_3 substitution on phosphorus from three to two by the addition of dimethyl amine, which was previously demonstrated for $(CF_3)_3P$ and $(CF_3)_3PO$, has now been shown to occur with $(CF_3)_3PS$. The only remaining conversions which have not yet been commonly observed are those between the mono- and di- CF_3 substituted phosphines. Future work on these systems might include development of a method to accomplish these conversions, extended studies of CH_3I addition to the tetramer, pentamer mixture and further study of CH_2I_2 additions to P-P bonds.

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